



GEOCHEMICAL STUDY OF THE KUMPULA CAMPUS
DRILL CORE AND OUTCROPS:
APPLYING A PORTABLE XRF DEVICE FOR WHOLE ROCK
ANALYSIS

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<p>Tiivistelmä/Referat – Abstract</p> <p>As a part of Kumpula Campus Drill Hole Project, a 370 m deep drill hole was drilled on the University of Helsinki, Kumpula campus area in December 2015. Drilling took place on an amphibolitic outcrop, which is the main rock type of the area and part of the 1.9 Ga old Svecofennian orogenic belt.</p> <p>In this work, the geochemistry of the campus bedrock is analyzed, focusing on the amphibolite. Granite, actinolite rock and diopside-actinolite skarn are additional rock types described from the core in this work. The geochemical methods utilized are a portable X-ray fluorescence (P-XRF) spectrometer Niton XL3t GOLDD+ by Thermo Scientific and a laboratory wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer PANalytical Axios mAX 4kW. WD-XRF device is utilized in quantitative analysis and semi-quantitative Omnian scans. In addition to geochemical interpretation of the bedrock, feasibility of the P-XRF device in outcrop and drill core related studies is evaluated by comparing the methods.</p> <p>The surface of the drill core was analyzed with the P-XRF device. Representative samples of each rock type were sawed of the core and analyzed with both P-XRF and WD-XRF Omnian scans. In addition to surface analyses, a fused bead was prepared from one representative amphibolite sample and analyzed with WD-XRF quantitative method. Outcrop studies focused on the feasibility of the P-XRF device in <i>in situ</i> analyses.</p> <p>Compared to nearest temporally related amphibolite units, the amphibolite of the campus bedrock seems to be more felsic on average. All described rock types are connected to former petrogenetic interpretations of the local bedrock. However, further geochemical analyses are required to verify the interpretations. WD-XRF quantitative method and Omnian scans suggest almost similar results for fused bead of the amphibolite. Changing the sample type to solid rock surface introduces heterogeneity related problems to the quantitative determination of Omnian scans and quality of the results decreases almost to the level of P-XRF. Yet, the advantage of the Omnian scans method in rock surface analyses compared to P-XRF is better detection of light elements. For example, P-XRF device detects Mg, Al and K poorly and Na is not detected at all. On the other hand, SiO₂ is on average detected quite accurately from rock surface with P-XRF when compared to WD-XRF quantitative method for fused bead. WD-XRF Omnian scans and quantitative application results of fused bead do not seem to differ remarkably. Broad rock type classification can be made with P-XRF device for drill core, but results cannot be considered quantitative. It should also be noticed, that the major element oxide sum values of P-XRF drill core surface analyses are quite low on average (84.00 wt.%). In outcrop analyses, different features lower the quality of the rock surfaces, resulting in even lower major element oxide sum values in analysis. Although major oxide sum values are very low on outcrops, relatively high amounts of for example Cl, S and P are detected for unknown reasons.</p> <p>Major advantages of the P-XRF device are the ease of use, light weight and rather good detection of for example SiO₂. Developing the quantitateness of the device would make it more comparable to laboratory XRF devices but it already has multiple features that are highly beneficial in a wide range of scientific fields.</p>			
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<p>Tiivistelmä/Referat – Abstract</p> <p>Osana Helsingin yliopiston Kampusreikä projektia, vuonna 2015 Kumpulan kampuksen kallioperään porattiin 370 m syvä kairareikä opetustarkoitukseen. Kampuksen kallioperän pääkivilaji on paleoproterotsooinen, n. 1.9 Ga vanha amfiboliitti. Tässä työssä amfiboliitin geokemiaa selvitetään Thermo Scientificin Niton XL3t GOLDD+ kannettavan röntgenfluoresenssi laitteen (P-XRF), sekä laboratoriokäyttöisen aallonpituusdispersiivisen röntgenfluoresenssilaitteen (WD-XRF) avulla. WD-XRF-analysointia hyödynnetään kvantitatiivista menetelmää sekä semi-kvantitatiivista Omnian menetelmää. Geokemian ohella P-XRF-laitteen käyttöä arvioidaan XRF menetelmiä vertaillen. Amfiboliitin lisäksi kairasydäimestä kuvailtiin graniitti, aktinoliitti kivi ja diopsidi-aktinoliitti karsi.</p> <p>Kampusreikästä saadun kairasydämen pintaa analysoitiin P-XRF-laitteella. Lisäksi siitä saatiin edustavat näytteet jokaisesta kuvaillusta kivilajista ja näytteiden pinnat analysoitiin sekä P-XRF, että WD-XRF Omnian-metodeilla. Yhdestä edustavasta amfiboliittinäytteestä analysoitiin pinta P-XRF-laitteella sekä WD-XRF Omnian-menetelmällä, ja lisäksi siitä valmistettiin fluksinappi, joka analysoitiin sekä WD-XRF Omnian-menetelmällä, että kvantitatiivisella WD-XRF-menetelmällä. Paljastuma-analyysien avulla tutkittiin lähinnä <i>in situ</i> P-XRF-mittausten onnistumista vallitsevissa olosuhteissa.</p> <p>Amfiboliitti on tulostensa perusteella felsisempi kuin läheiset saman ikäiset amfiboliittiyksiköt. Kaikkien kivilajien tarkempi kuvailu vaatii kuitenkin lisää geokemiallisia analyysejä. Eri XRF-menetelmien tuloksia vertaillaessa todetaan näytetyypin valinnalla olevan huomattava vaikutus tuloksiin. Sahattujen näytteiden pinta-analyysissä WD-XRF Omnian-menetelmän etuna on parempi kevyiden alkuaineiden (Mg, K ja Al) rekisteröityminen verrattuna P-XRF-menetelmään. Natriumia P-XRF-laite ei rekisteröi ollenkaan. P-XRF-menetelmä kiven pinnasta antaa keskimäärin melko oikean pitoisuuden SiO_2:lle, kun verrataan kvantitatiivisen analyysin tulokseen fluksinapista. WD-XRF Omnian-menetelmän ja WD-XRF kvantitatiivisen menetelmän tuloksilla ei ole juurikaan eroa fluksinappianalyysissä. Karkeita kivilajivaihteluita pystytään havaitsemaan P-XRF-laitteella kairasydäimestä, eikä WD-XRF Omnian-menetelmä välttämättä tuo tämän tyyppiseen tutkimukseen lisäarvoa. P-XRF-menetelmää ei kuitenkaan voi pitää kvantitatiivisena. Huomioitava seikka on myös se, että P-XRF-menetelmän pääalkuaineoksidien summat jäävät alhaisiksi kairasydämen pinnan analyysissä (k.a. 84.00 p.%). Paljastumilla arvo putoaa entisestään, ja pintojen huono laatu osoittautuu suurimmaksi ongelmaksi. Vaikka pääalkuaineoksidien summa on hyvin alhainen, niin esimerkiksi Cl, S ja P esiintyvät suhteellisen korkeina pitoisuuksina paljastumilla, toistaiseksi tuntemattomista syistä.</p> <p>P-XRF menetelmän eduiksi voidaan todeta erityisesti sen helppokäyttöisyys, liikuteltavuus ja esimerkiksi SiO_2 pitoisuuden melko todenmukainen rekisteröityminen. Laitteen kvantitatiivisuuden kehittäminen nostaisi sen kilpailukykyä tarkkojen laboratoriolaitteiden rinnalla, mutta tähän asti saavutetuista ominaisuuksista on jo nyt paljon hyötyä esimerkiksi kairasydäntutkimuksissa.</p>			
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1. INTRODUCTION

1.1 Kumpula Campus Drill Hole Project

In 2015, an opportunity to take a closer look of the Kumpula campus bedrock (Fig. 1) occurred, when the Kumpula Campus Drill Hole Project started. The Project aims to produce scientific data of the bedrock and serve as an environment for pre-graduate drill hole and core related education in geosciences in the Kumpula campus (Kukkonen et al. 2016). The drilling contractor Suomen Malmi Oy operated the diamond core drilling in December 2015, on an outcrop south of Dynamicum building (Fig. 1.C). The drill hole is 370 meters long and dips towards northeast with a dip of 70 degrees (Kukkonen et al. 2016). The diameter of the core is 56 mm and that of the drill hole 76 mm.

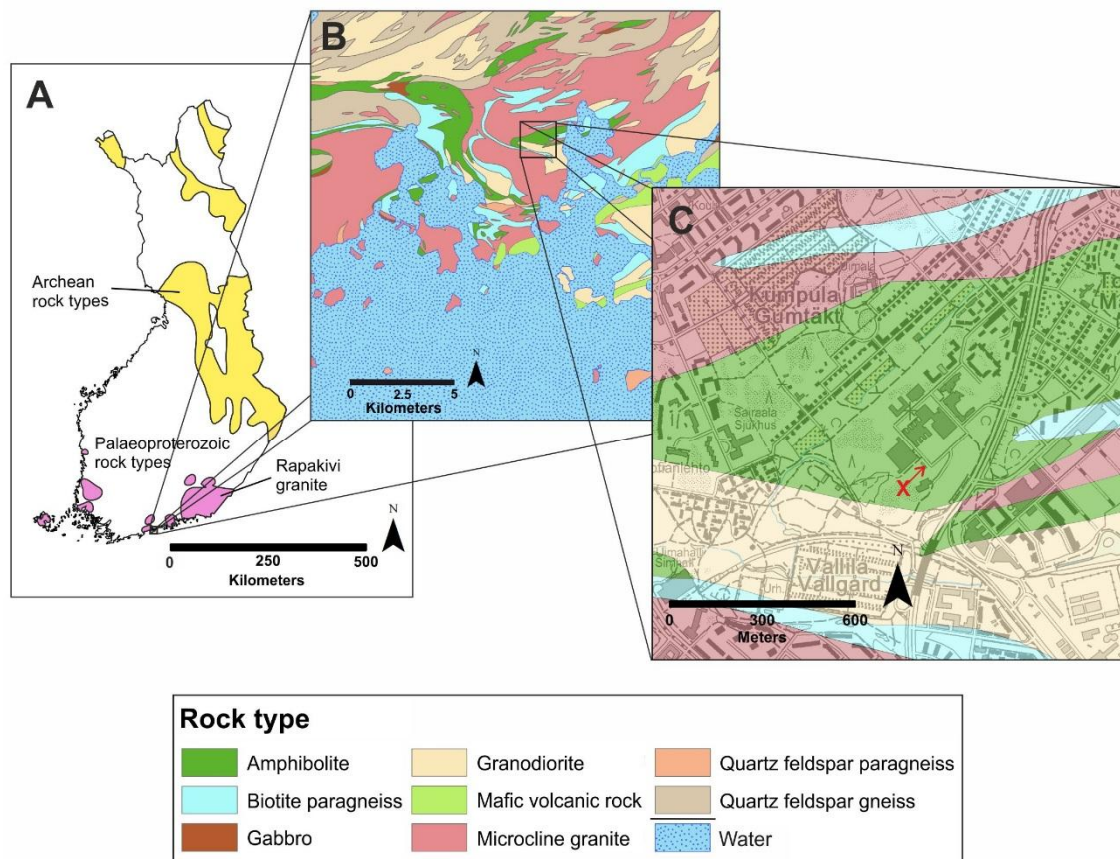


Figure 1.A: Location of Helsinki and major bedrock units of Finland (after Korsman and Koistinen 1998). B: Versatile bedrock of the Helsinki coast. C: Kumpula campus area bedrock. Dark gray campus buildings can be seen in the center of the map. Red X and arrow mark the drilling site and surface projection. B and C bedrock maps modified after Geological survey of Finland, abbr. GTK. Basemap of Finland in A and B © National land survey of Finland, abbr. NLS. City map of Helsinki in C © NLS.

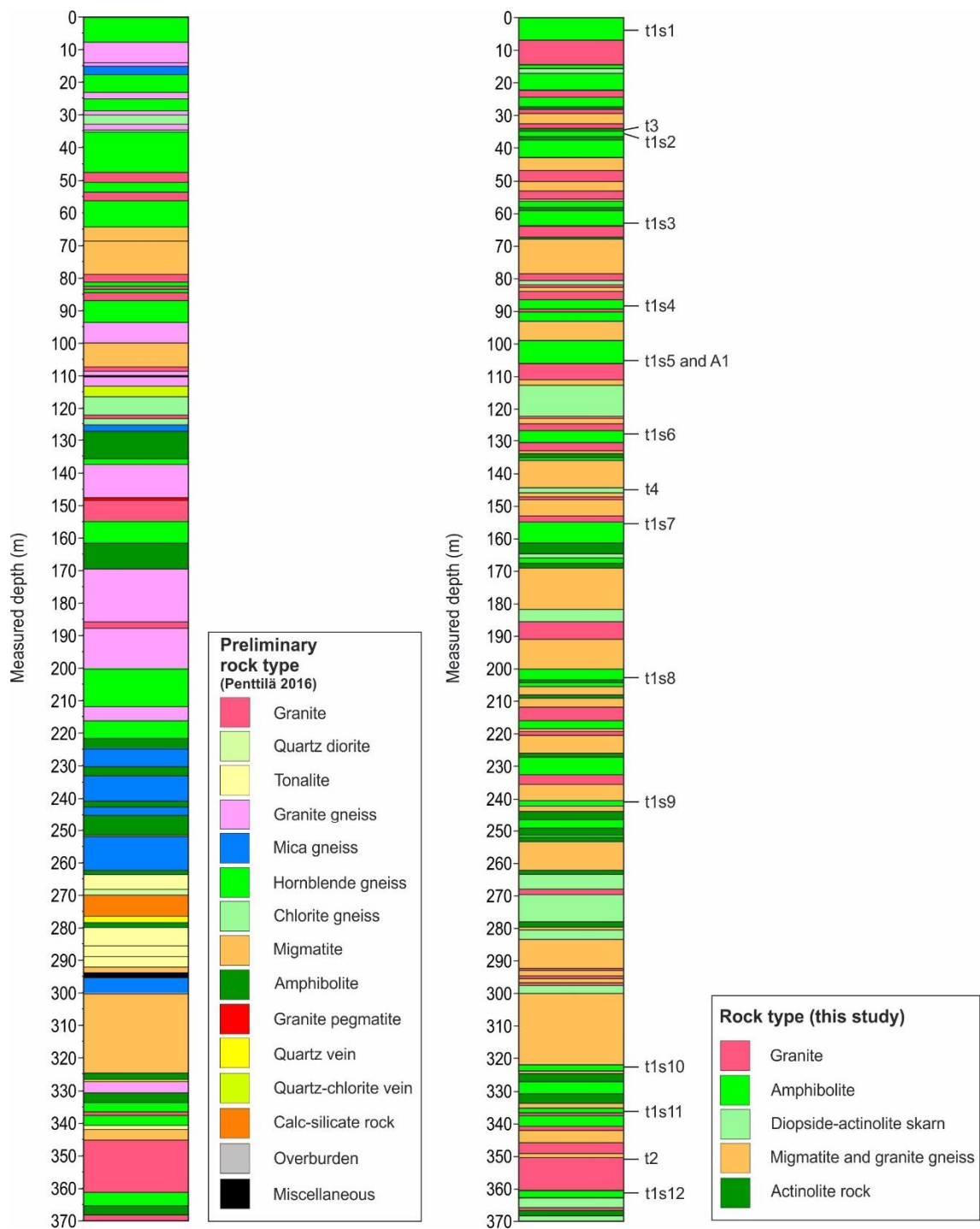


Figure 2. Preliminary rock type classification of the drill core according to Penttilä (2016) and a simplified classification used in this work. Depths of WD-XRF analysis spots are marked next to the core. WD-XRF Omnicar scans IDs: Amphibolite t1s1–t1s12, granite t2, actinolite rock t3 and diopside-actinolite skarn t4. WD-XRF quantitative application analysis of the amphibolite marked as A1.

Preliminary master's thesis studies in geology utilized the drill core and hole in fracture mapping and 3D-modeling (Valtonen in prep.), petrology (Penttilä in prep.) and

geochemistry. Figure 2 shows the preliminary division of the drill core rock types (Penttilä 2016) and a simplified classification used in this work.

In addition to drill core, an extensive set of wireline geophysical logs ran by GRM-Services Oy are available to support geological studies. The geophysical parameters include optical imaging, acoustic imaging, rock resistivity (several methods), self-potential, IP effect, magnetic susceptibility, gamma ray spectroscopy (U, Th and K), total gamma, gamma-gamma density, fluid temperature and fluid electrical conductivity (salinity) (Kivinen 2016).

1.2 Geological setting

Kumpula campus, University of Helsinki is situated in southern Finland (Fig. 1.A). The bedrock of Helsinki and the whole southern and western Finland are composed of the roots of a mountain range belonging to Palaeoproterozoic Svecofennian orogenic belt, which had its peak point of orogeny at about 1.9 Ga (Laitala 1991).

The orogeny was a result of an active Svecofennian island arc system obliquely colliding against the Archaean continent. Because of the complexity of the collision, Pajunen et al. (2008) have divided it to multiple geotectonic events, deformation phases and related rock series. Simplifying, the evolution of the Svecofennian orogeny 1.90–1.87 Ga consists of a N–S trending compression and a southward migrating, local extension (Pajunen et al. 2008).

The extension events caused strong vertical shortening and prograde high-T/low-P metamorphism resulting in some of the originally sedimentary and volcanic rocks metamorphosing to mica-bearing gneisses, hornblende gneisses and amphibolites. Plutonic rocks of Svecofennian age usually conform to the structures of volcanic rocks. The late-orogenic granites intruded the pre-existing bedrock and are usually mixed with other rock types thus forming gneisses, migmatites and breccias (Laitala 1991, Nironen 1998, Pajunen et al. 2008).

The Kumpula campus buildings are situated on a Proterozoic amphibolite unit with a minor part of the outcrop south of the buildings belonging to a granodiorite unit (Fig. 1.B and 1.C).

1.3 Aim of the study

During the previous decades, the increasing interest towards the portable X-ray fluorescence (P-XRF) spectrometer has resulted in fast technological development. The non-destructiveness and fastness of the analyses are advantageous properties in a wide variety of scientific fields. P-XRF devices have already been tested and utilized in e.g. detecting metals in pre-concentrated aqueous samples (Marguí et al. 2012), detecting hazardous substances in soils (Markey et al. 2008, Parsons et al. 2013, Hatakka et al. 2016), mineral exploration (Sarala et al. 2014), chemostratigraphy (Rowe et al. 2012), archaeology (Liritzis and Zacharias 2011), industrial quality control (Shrivastava et al. 2005), and in the future will also be utilized in planetary surface explorations (Young et al. 2016).

As the Niton XL3t GOLDD+ P-XRF spectrometer by Thermo Scientific is a quite new (2015) purchase in the Department of Geosciences and Geography, major part of this work aims to evaluate the feasibility of the P-XRF device in *in situ* outcrop studies and drill core related studies. With the help of drill core and outcrop data, the geochemical characteristics of especially the amphibolite of the campus bedrock are examined. In the process the P-XRF method is compared to laboratory wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer PANalytical Axios mAX 4kW.

Thus, the geochemical data obtained with different XRF methods serve, not only as a window to the geochemical composition of the bedrock, but as a ground for P-XRF – WD-XRF comparisons. Major element oxide results were selected as the most reliable data for identifying the differences between the XRF methods. Together with fracture information (Valtonen in prep.) and an extensive petrology interpretation (Penttilä in prep.) the ongoing master's thesis projects form a comprehensive survey of the Kumpula campus bedrock.

2. METHODS

The X-ray fluorescence spectroscopy is based on non-destructive exciting and detecting of characteristic secondary X-rays (*fluorescence*) of different elements in a sample (Norrish and Chappell 1967). By detecting the fluorescence intensities, it is possible to identify the elements and evaluate their proportions. Fluorescence is excited by radiating the sample with high intensity X-rays (Norrish and Chappell 1967, Potts and Webb 1992). Main differences of the two methods used in this work are related to fluorescence detection and are described in the following chapters.

Both spectrometers belong to the Department of Geosciences and Geography, University of Helsinki. In addition to XRF analyses, a brief petrography work was done for each described rock type to get a better picture of the mineral compositions.

2.1 WD-XRF

WD-XRF devices are wavelength dispersive, which means that the emitted sample fluorescence is directed to the detector via a synthetic analyzing crystal, which disperses the fluorescence spectrum (Norrish and Chappell 1967). Adjusting the angle between crystal and detector, multiple wavelengths can be detected, individually. Collimators are placed between the X-ray tube and the sample and between the sample and the detector to direct the primary X-rays and fluorescence (Marguí 2013). The diffraction and collimation weakens the fluorescence intensity and analysis is also much slower than with P-XRF device, but resolution remains high (Marguí 2013). High resolution allows lower detection limits and thus better identification of trace elements than with P-XRF device (e.g. Potts and Webb 1992). WD-XRF analyzer used in this work is PANalytical Axios mAX 4kW.

2.1.1 Quantitative application

The quantitative WD-XRF application was utilized for one fused bead analysis. The quantitative calibration uses international certified reference samples of 19 different natural compositions for detecting the elements (Heikkilä 2015) and has also a fixed

fundamental parameters (FP) model that corrects matrix effects calculated for on an average granodioritic composition (Pasi Heikkilä, pers.comm. 2018). FP model considers fluorescence of all orders, physical constants and multiple instrumental features (Marguí 2013).

2.1.2 Omnian scans

Along with quantitative application, PANalytical's semi-quantitative method called Omnian was utilized for all sawed rock surface analyses and for the fused bead analysis. The standardless Omnian scans method is calibrated using matrix independent setup samples (PANalytical 2018). Elements from O to U can be detected using multiple analyzing crystals. The quantification uses a software that has advanced FP model algorithms compared to quantitative application (PANalytical 2018). The model has variable features that are calculated individually for each setup sample and unknown sample (Pasi Heikkilä, pers.comm. 2018). Background profile fitting and peak search is based on theoretical peak database (Heikkilä 2015). In the end, the software converts elemental peak intensities to elemental concentrations and thus theoretical composition is obtained. Omnian method also allows the user to correct the kV-kcps spectrums received from the analysis, if necessary.

2.2 P-XRF

Portable XRF devices exploit energy dispersion (ED) directly by simultaneously detecting all wavelengths of the fluorescence (e.g. Kramar 1997). Comparing to collimated fluorescence obtained with WD-XRF, ED-XRF detector views a wider range of polychromatic fluorescence (Potts and Webb 1992). The resolution especially in the lower energies of the spectrum is poor (Potts and Webb 1992), and the method is thus at best semi-quantitative for most elements. However, simpler instrument with less delicate parts compared to WD-XRF makes fast qualitative (elemental range from Mg to U) and semi-quantitative analyses possible with a miniaturized apparatus (Marguí 2013). Depending on the sample type to be analyzed, there are multiple different kinds of P-XRF devices optimized for different purposes. Different softwares also expand the use of the device as new calibrations are added.

The portable XRF device used in this work is Niton XL3t GOLDD+ (50kV) by Thermo Scientific with a round analysis window diameter of 8mm. In all the analyses the analysis mode was set to “Mining Cu/Zn” and the analysis time was fixed to 100 seconds to optimize the detection time required for different elements. The device was held in hand during all analyses.

3. MATERIALS AND SAMPLE PREPARATION

3.1 Drill core

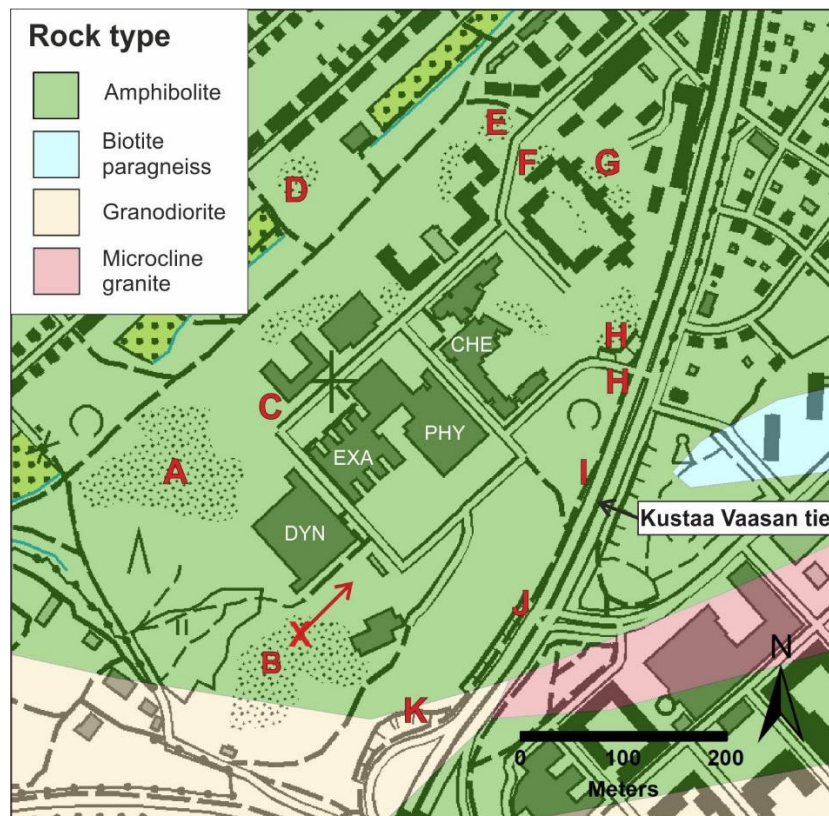


Figure 3. Locations of the selected outcrops in relation to Kumpula campus buildings. The selected outcrops are named with letters A–K. Red X and arrow mark the drilling site and surface projection of N-E trending drill hole. Abbreviations: DYN=Dynamicum, EXA=Exactum, PHY=Physicum and CHE=Chemicum. Bedrock map after GTK and basemap © NLS.

The drilling took place in the Kumpula campus area, on an amphibolite outcrop (Outcrop B, Fig. 3) south of Dynamicum building. The complete set of 82 boxes containing the 370 meter long drill core is stored in the basement of Physicum building.

All referenced depths regarding the drill core in this work are measured depths along the core and not precise vertical depths.

Before geochemical analyses, the core was visually examined to preliminarily define different rock types and other features like fractures. There were two major fracture zones in depths 108.80–110.20 m and 294.40–295.20 m. Other than that, the core is rated excellent in rock quality designation (RQD) (Valtonen in prep.).



Figure 4. An example of the drill core from depth ~118–127 m. Wet drill core shows high variation in rock type. The core in this figure has for example skarn, granitic veins, granitic gneiss, amphibolite and actinolite rock.

Four different main rock types were determined by simplified visual estimations: amphibolite, granite, actinolite rock and diopside-actinolite skarn (Fig. 4). Details of these rock types are presented in Chapter 4. Closer description of the core is presented in petrology studies by Penttilä (in prep.). Despite the relatively high amount of variation in rock type (Fig. 2 and Fig. 4), amphibolite was chosen to be in the center of attention in the present study. The relatively small grainsize of the amphibolite was considered to increase the suitability for direct XRF analyses and therefore most of the analyses are focused on it (Table 1).

In addition to the four rock types described above, large part of the core is migmatite and gneiss of various compositions. Their wider examination was not considered meaningful for this work, however.

Table 1. Total number of core analyses with each method of each rock type.

	Amphibolite	Granite	Actinolite rock	Diopside-actinolite skarn
Core surface, whole length				
P-XRF	38	46	27	29
Sawed core pieces				
Rock surface:				
P-XRF	12	1	1	1
WD-XRF Omnian scans	12	1	1	1
Amphibolite sample A1				
Rock surface:				
P-XRF	20			
WD-XRF Omnian scans	1			
Fused bead:				
WD-XRF quant.app.	1			
WD-XRF Omnian scans	1			

3.1.1 P-XRF core surface analyses

Every major rock type unit was analyzed with P-XRF at least once, depending on the thickness of the unit. Best way to perform the analyses turned out to be to place the analysis window tightly against the curved surface of the core. This way the distance between the apparatus and rock surface was minimized and escaping of the X-ray beam and fluorescence best avoided. The core was analyzed without removing it from the containers. Based on drill core results, variation in geochemistry and rock type with depth are later evaluated.

3.1.2 Sawed pieces

To compare the P-XRF and WD-XRF methods, fifteen representative, round pieces (each ~2 cm thick) were sawed out of the drill core: twelve amphibolites, one granite, one actinolite rock and one diopside-actinolite skarn. Sample pieces did not require additional preparations as the diameter of the core was already small enough to fit in the sample holder of the WD-XRF device. Sawed surfaces of the pieces were analyzed first

with P-XRF and then utilizing WD-XRF Omnian scans. Before WD-XRF analyses, sample pieces were cleansed with VWR Ultrasonic Cleaner that uses ultra sound. Pieces were placed in distilled water at room temperature for 20 minutes. In WD-XRF device, the power was set to 3kW and analysis surface to 27 mm in diameter. Sample type was selected as “Solid compounds”.

One extra piece of amphibolite (sample A1) from depth 105.35 m was sawed in half parallel to the core length and analyzed multiple times with the P-XRF device: ten times from the curved core surface and ten times from the straight sawed surface. This way the heterogeneity of the amphibolite sample and the effect of surface curvature were examined. The remaining half of the piece was melted into fused bead and analyzed with WD-XRF quantitative method and Omnian scans.

3.1.3 Fused bead

Sample preparation and WD-XRF studies were carried out at the Mineralogy laboratory of Kumpula campus, University of Helsinki. Preparing the fused bead started with crushing the sample with a jaw crusher (Suomen Teräsrakenne Oy MKH press, model CMT 100/150, 4kW). The previous rock type in the crusher had been granodiorite. After crushing, the sample pieces were heated in a Teflon cup at 105 °C for about 24 hours to remove volatiles. Then 30 g of representative fractions were picked and pulverized with Fritsch PULVERISETTE 6 ball mill. Sample fractions were pulverized in a tungsten carbide pan, with three tungsten bullets and few droplets of ethanol for 15 minutes, at around 350 rpm.

The process continued then with measuring 0.6 g of pulverized sample in a Au-Pt crucible. Then the flux was added: total of $6.0 \text{ g} \pm 0.001 \text{ g}$ of $\text{Li}_2\text{B}_4\text{O}_7$ (49.75 %), LiBO_2 (49.75%) and LiBr (0.50%). After adding the fluxing agent, total weight of the sample was 6.6 g. The sample was then melted with Claisse M4 burner at 1000 °C for 1700 seconds and after that poured into Au-Pt mold to cool. Throughout the preparation of the fused bead the Mineralogy Laboratory Manual (Heikkilä 2015) instructions were followed.

3.2 Outcrops

The surroundings of the campus were explored by selecting a total of eleven representative outcrops around the campus during the summer of 2016. In the Figure 3 the selected outcrops are named with letters A–K. The most important factor, when deciding which outcrops were to be analyzed, was finding surfaces that qualify for the P-XRF analyses. The success of each analysis was evaluated directly with the help of major element oxides sum.

Features increasing the surface suitability were considered to be for example cleanness, small grain size, solidity and smoothness. The impact of these features on the results are further examined by comparing good quality and poor quality surfaces occurring next to each other. Poor quality surfaces were covered in lichen, moss or pollution and/or were weathered. Without further biological or chemical examination, poor quality surfaces were not classified by detail and were treated as one group.

According to the GTK bedrock map, the campus area is situated in an amphibolitic lithological unit with granite, biotite paragneiss and granodiorite units nearby. Field observations support the GTK interpretation. Major rock type was found to be amphibolite with grain size of ~2 mm in diameter, but varying even inside one outcrop. Usually mafic minerals were notably elongated. In addition to varying grain size, composition and color varied as well and thus deciding the name between granitic gneiss/hornblende gneiss/migmatite/amphibolite was not straightforward.

Pink granitic veins crossing amphibolite were coarse and of various thicknesses, thickest being ~1 m in diameter (found on Outcrop D, Fig. 3). Fine grained, mafic dike crossed part of outcrop H and was not found on any other outcrop.

The representativeness of different rock types in the outcrop analyses was completely dependent on the applicability of the P-XRF method. The purpose of the outcrop analyses was to analyze the surfaces *in situ* without any sample preparation, other than removing the most notable debris off the surfaces. In few cases, a fresh surface was chipped with a hammer. This was easiest along Kustaa Vaasan tie (Fig. 3), where the outcrops are vertical road cuttings. Depending on each outcrop size and suitability for

the P-XRF analyses, one or more analyses on each and a total of 114 analyses were conducted in the surroundings of the campus with the P-XRF device.

4. PETROGRAPHY

The petrographic examinations were done for four thin sections prepared from the drill core. The selection of these particular samples were determined by their representativeness of each different main rock type described for the drill core. The 30 µm thick, polished thin sections were examined with Nikon Labophot-2 Pol polarizing microscope.

The following description of each sample includes macroscopic description, microscopic description, mineral assemblage listed and possible special features. Photographs and photomicrographs of the samples are presented with individual descriptions for each rock type. Photographs include a picture of the hand sample and magnified pictures of the thin sections in plane-polarized light (PPL) and cross-polarized light (XPL).

Mineral abbreviations in photomicrographs after Kretz (1983):

Act = actinolite

Ap = apatite

Bt = biotite

Pl = plagioclase

Hbl = hornblende

Qtz = quartz

Kfs = K-feldspar

Ttn = sphene (titanite)

Zo = zoisite

Tr = tremolite

Ep = epidote

4.1 Amphibolite

Representative sample of the area's main rock type, amphibolite, is from the depth of 36 m. Hand specimen seems quite dark and even-grained, grain size being about 1 mm in diameter (Fig. 5.A). With naked eye, a preferred orientation is clearly visible in thin section. One light colored vein crosscuts the sample.

Main minerals include abundant hornblende (~50%), plagioclase (~25%) and quartz (~15%) (Fig 5). Biotite occurs as an accessory mineral, along with zircon and apatite (together ~10%). Plagioclase has multiple twinning and is partly altered to sericite (Fig. 5.B and 5.C). Such secondary alteration can be seen especially around the vein.

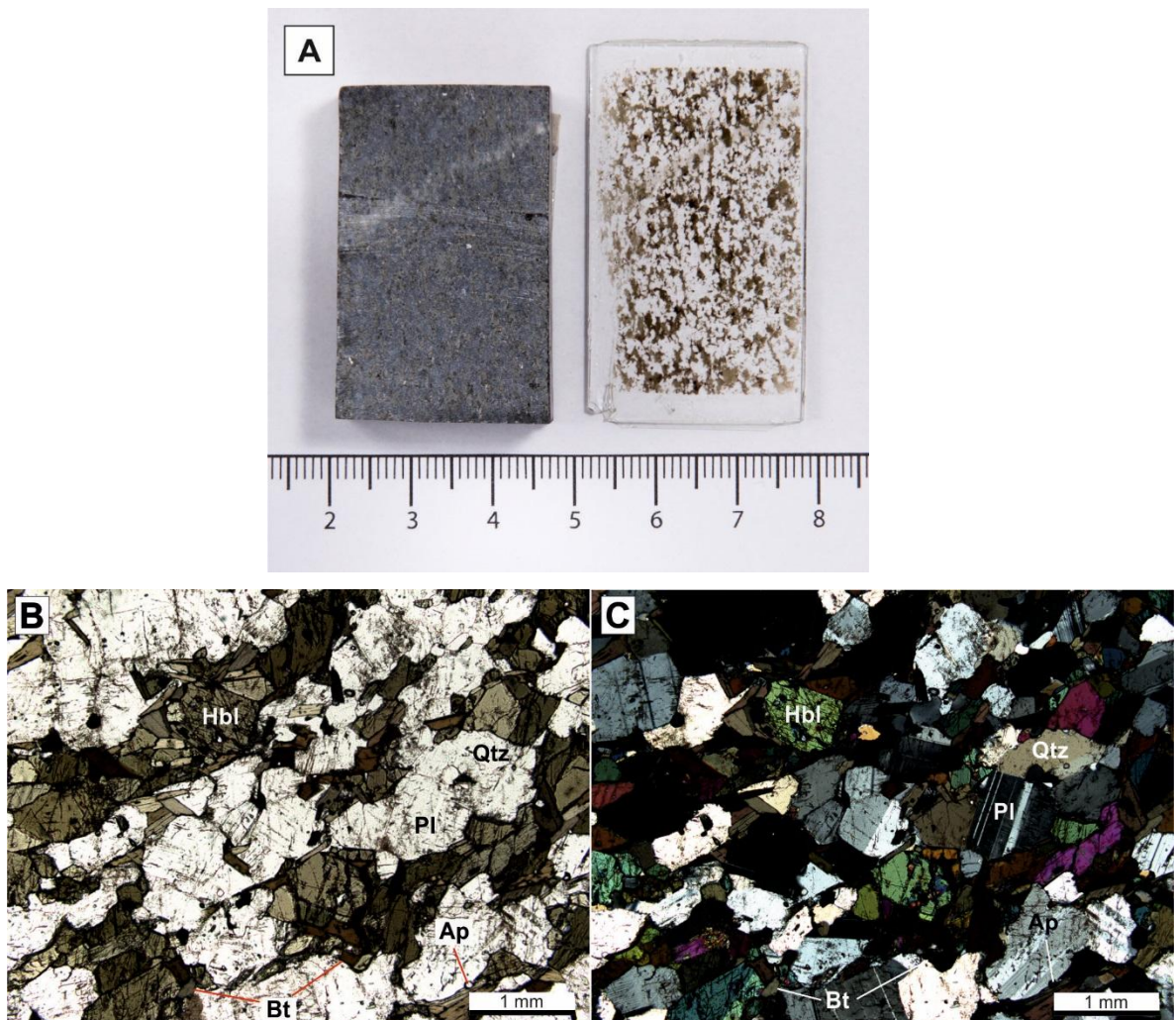


Figure 5.A: Hand specimen is even-grained and dark gray in color with grain size about 1 mm in diam. Light colored vein crosscuts the sample. Thin section shows clearly the dark green amphibole. B: Thin section with 2.5X magnification in PPL: Transparent grains are mainly plagioclase and quartz. Green minerals are amphibole and also some biotite is present. C: XPL: Amphibole shows first order colors and plagioclase multiple twinning.

4.2 Granite

Granite sample is from the depth of 351.50 m. Hand specimen is reddish and even-grained with grain size of ~2mm in diameter (Fig. 6.A). With naked eye, thin section seems felsic and without a preferred orientation.

Quartz (~35%) exhibits undulating crystal boundaries and some of the crystals show undulose extinction. Plagioclase (~25%) is partly altered to sericite. Potassium feldspar (~30%) shows cross-hatched microcline twinning and perthite. Accessory minerals include biotite that is in some places altered to chlorite. Epidote is also present in minor amounts and is always associated with biotite (together ~10%) (Fig. 6).

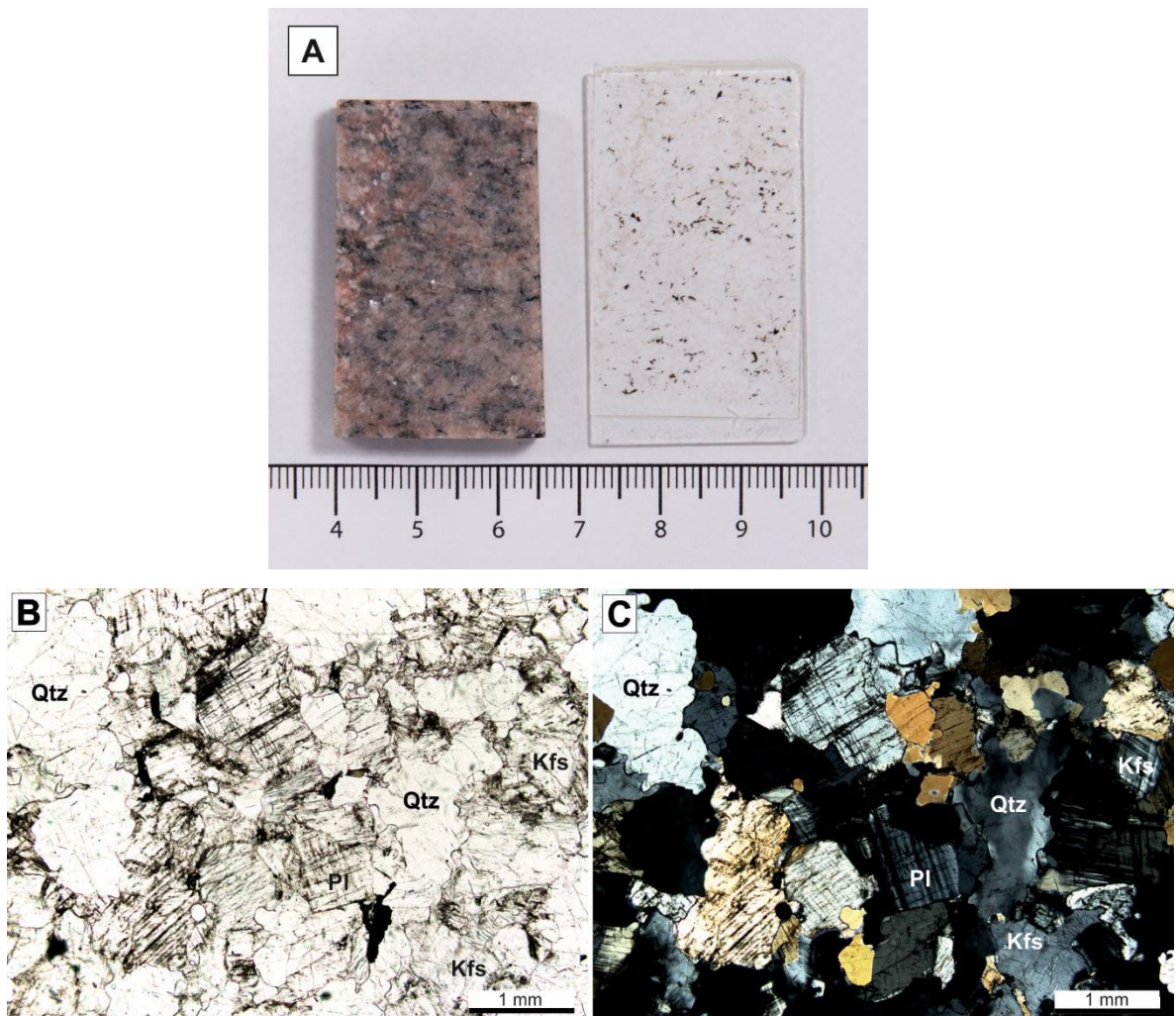


Figure 6.A: Hand specimen of the granite sample seems reddish with a grainsize of 1–2 mm. B: 2.5X magnification in PPL: the abundance of felsic minerals is clear. Sericite dims the feldspar crystals. C: In XPL only first order colors are visible. Quartz shows undulose extinction and undulating crystal boundaries.

4.3 Actinolite rock

Actinolite rock sample is from the depth of 35 m. Rock has a clear preferred orientation. Clusters of biotite crystals are clearly visible with naked eye in thin section. The material between the clusters is light green in color (Fig. 7.A).

Biotite (~40%) shows very faint light brown pleochroism (Fig. 7.B). Largest crystals are 0.5 cm in diameter. Crystal boundaries have strings of high relief crystals with halos. These are too tiny to be recognized. Between biotite crystals and crystal clusters, there are actinolite crystals (~60%) that are slightly pleochroic from pale green to white. Actinolite crystals are anhedral and <0.5 mm in diameter. No other minerals are present and this rock is probably of metasomatic origin (Fig. 7).

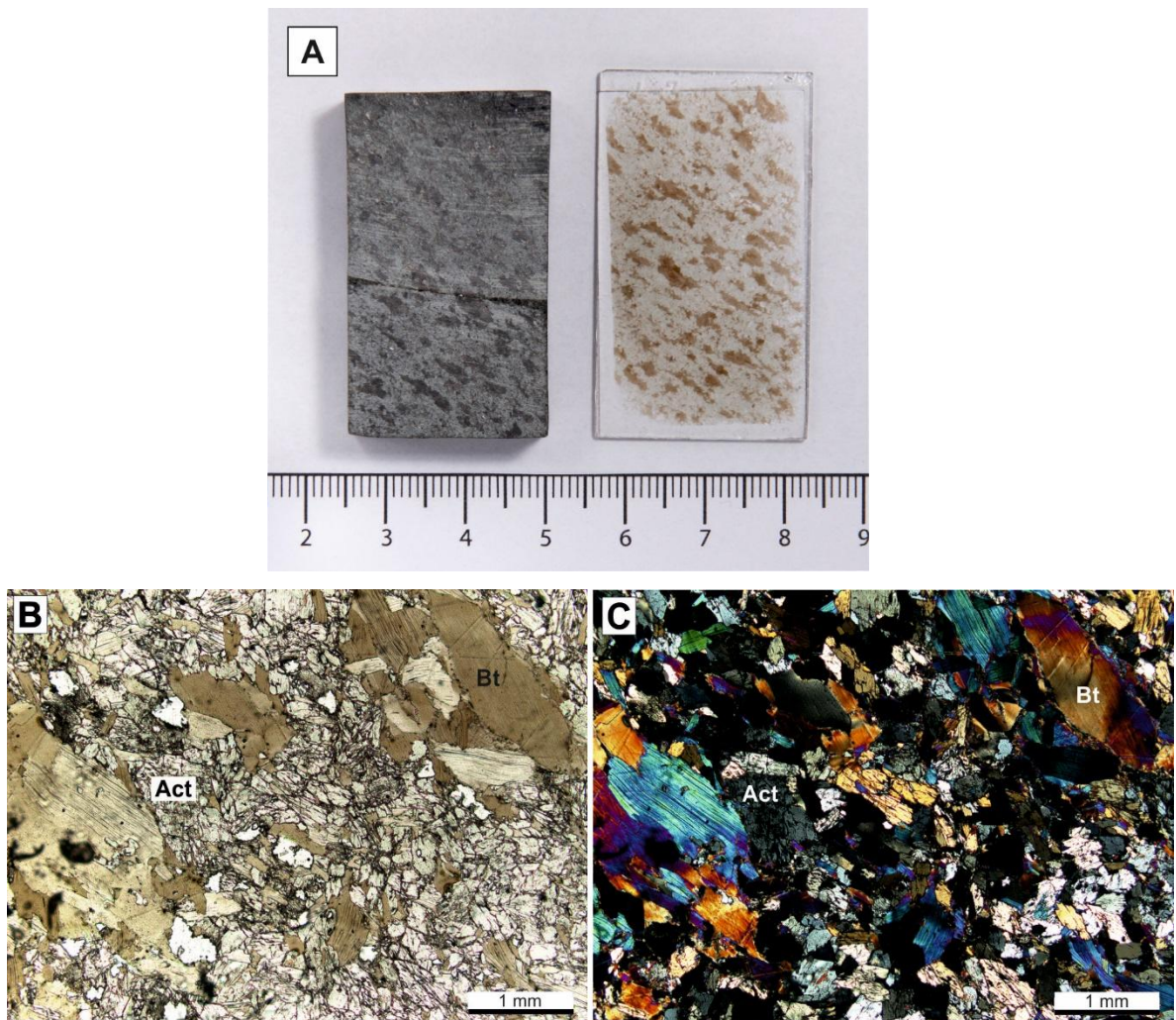


Figure 7.A: Hand specimen of actinolite rock is dark green and clearly oriented. Thin section shows the brownish pleochroism of biotite clusters. B: PPL and C: XPL 2.5X magnification reveals the variation in grainsizes: biotite grains are even multiple mm long, and smaller actinolite crystals fill the spaces between biotite clusters.

4.4 Diopside-actinolite skarn

Diopside-actinolite skarn is from the depth of 145.70 m. Hand specimen is greenish gray in color (Fig. 8.A). Grain size is about 1 mm in diameter and the rock is even-grained. One dark green filled fracture crosscuts the sample. Minerals have no preferred orientation. Thin section looks almost completely colorless with an unaided eye.

Plagioclase (~50%) is strongly altered to sericite in some parts, especially around the filled fracture crosscutting the sample (Fig. 8.F, 8.G). Plagioclase composition is andesitic in unaltered crystals and albitic in altered crystals on the basis of the extinction angle of the twinning. Diopside (~30%) is present as subhedral crystals. Actinolite (~10%) occurs as euhedral/subhedral crystals with slightly yellow/light green color in PPL. Sphene (~5%) occurs as an accessory mineral throughout the sample as small subhedral crystals. The fracture crosscutting the sample hosts tremolite, subhedral epidote and subhedral zoisite (together ~5%) (Fig. 8.B–8.G).

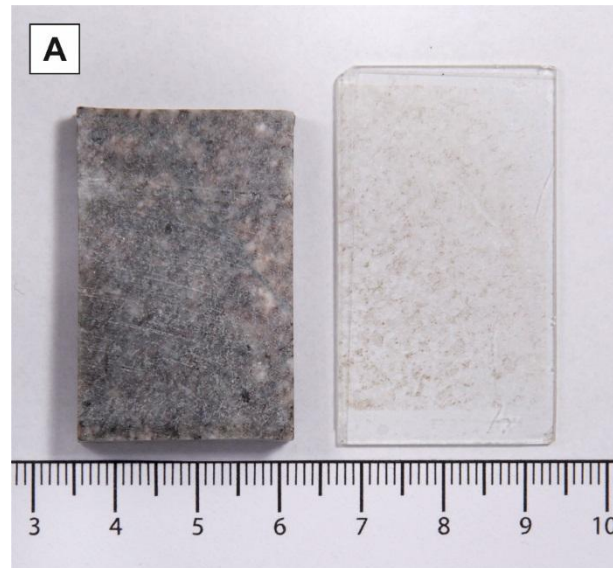


Figure 8.A. Hand sample and a thin section of diopside-actinolite skarn are quite faded in color and grain size is about 1 mm. The thin fracture crosscutting the sample has whiter colored, altered surroundings and a dark filling.

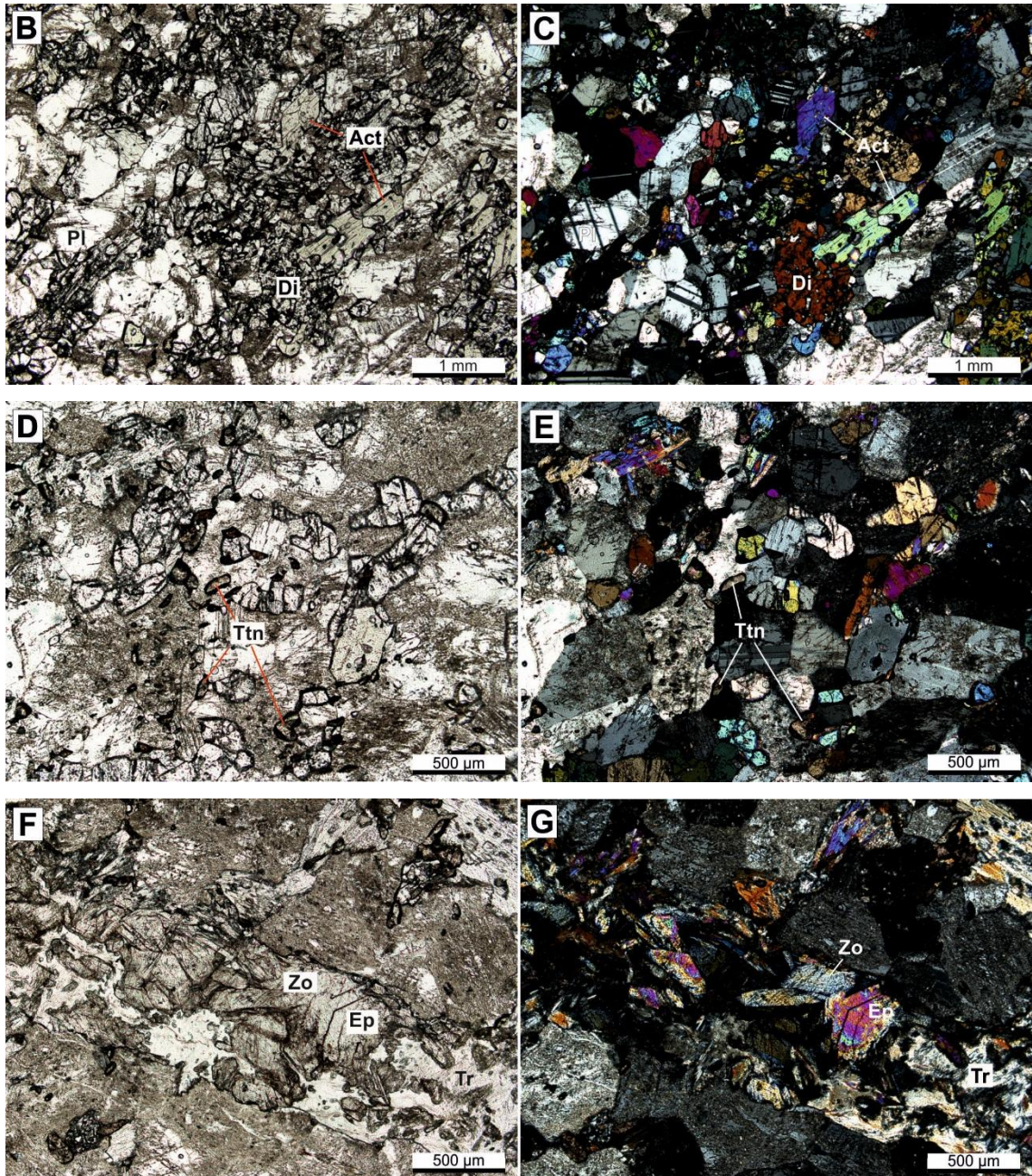


Figure 8. B and C: 2.5X magnification of the thin section shows slightly angular actinolite crystals, rounded diopside crystals and twinning in plagioclase. D and E: 5X magnification focuses on dark reddish brown sphene crystals that occur throughout the sample. F and G: 5X magnification of the fracture crosscutting the sample. Fracture hosts e.g. zoisite, epidote and tremolite.

6. RESULTS

Granite, actinolite rock and diopside-actinolite skarn whole rock geochemistry are fully based on WD-XRF Omnian scans from sawed rock surface analyses. The most quantitative result of the amphibolite with major element oxide sum of 98.13 wt.% was obtained with WD-XRF quantitative method of fused bead. These results together with

petrographic observations are considered first to interpret the petrology and petrogenesis of the Kumpula campus bedrock, focusing on the amphibolite. All presented values are untreated. Complete set of the results is tabulated in the appendices.

6.1 Whole rock geochemistry of the rock types

SiO₂ content of the selected rock types is highest in granite (72.04 wt.%) (Table 2). Granite has also relatively high K₂O content (4.23 wt.%) but less e.g. TiO₂ (0.08 wt.%), FeO_t (0.72 wt.%), MgO (0.35 wt.%) and CaO (1.20 wt.%) than other rock types. Actinolite rock has FeO_t (8.87 wt.%) and MgO (17.73 wt.%) contents that are distinctively high compared to other rock types. On the other hand, SiO₂ is only 43.19 wt.% and Na₂O 0.30 wt.%. Diopside-actinolite skarn shows high Al₂O₃ (18.15 wt.%) and CaO (10.59 wt.%) contents.

SiO₂ content of amphibolite is 57.41 wt.% (Table 2), which is equivalent to andesitic composition (Fig. 9) (Le Bas et al. 1986). K₂O wt.% together with Na₂O wt.% is 5.58 wt.%, which specifies the composition to andesite area, near the boundary of basaltic andesite (Fig. 9). More precise plotting of the WD-XRF quantitative result sets the rock type as an alkali basalt area according to the diagram by Pearce (1996), that uses Nb/Y and Zr/Ti ratios (Fig. 10) and thus eliminates the effects of alkali mobilization typical to metamorphic rocks. Amphibolite's TAS ratio plots to the sub-alkaline field and more precisely to medium-K field, which indicates calc-alkaline suite (Ewart 1982).

Degree of silica-saturation (Equation [1]) suggest the rock to be silica-oversaturated and Mg-number (Equation [2]) is less than that of primary magmas. Due to the lack of additional samples and more precise trace element and isotope data, further geochemical interpretation for amphibolite is not presented in this work.

Table 2. Whole-rock geochemical compositions of the four rock types of the Kumpula campus bedrock based on single analyses. Depths of the samples can be seen in Figure 2.

Rock type	Amphibolite	Granite	Actinolite rock	Diopside-actinolite skarn
Sample ID	A1	t2	t3	t4
Method	WD-XRF	WD-XRF	WD-XRF	WD-XRF
Sample type	Quantitative app. fused bead	Omnian scans rock surface	Omnian scans rock surface	Omnian scans rock surface
SiO ₂ (wt.%)	57.41	72.04	43.19	51.91
TiO ₂	0.97	0.08	0.58	0.68
Al ₂ O ₃	15.37	13.75	8.20	18.15
FeOt	7.50	0.72	8.87	1.35
MnO	0.12	0.02	0.17	0.04
MgO	4.93	0.35	17.73	5.33
CaO	6.06	1.20	7.30	10.59
Na ₂ O	3.93	4.08	0.30	4.30
K ₂ O	1.65	4.23	3.81	0.92
P ₂ O ₅	0.19	0.05	0.17	0.26
Sum	98.13	96.53	90.30	93.52
Ba (ppm)	415	360	140	200
Cl	n.a.	190	140	80
F	n.a.	n.d.	1390	n.d.
S	n.a.	60	60	50
Ce	48	n.d.	n.d.	n.d.
Co	n.a.	n.d.	70	n.d.
Cr	154	n.d.	2530	170
Cu	8	20	30	30
Ga	n.a.	20	20	20
La	19	n.d.	n.d.	n.d.
Nb	14	n.d.	n.d.	10
Ni	23	40	880	60
Pb	n.a.	40	n.d.	n.d.
Rb	72	180	270	40
Sr	292	80	10	320
U	4	n.d.	n.d.	n.d.
V	157	n.d.	150	180
Y	17	n.d.	n.d.	n.d.
Zn	65	10	100	30
Zr	78	70	50	90

n.a.= not
analysed

n.d.= not detected

Degree of silica saturation is calculated as following:

$$\frac{\left(\frac{SiO_2 \text{ wt.}\%}{60.08}\right)}{\left(\frac{Na_2O \text{ wt.}\%}{61.98}\right)} \quad [1]$$

=15.07 (> 6, rock is silica-oversaturated) for the representative amphibolite sample A1.

Magnesium number:

$$\frac{100 * \left(\frac{MgO \text{ wt.}\%}{40.30} \right)}{\left(\frac{MgO \text{ wt.}\%}{40.30} + \frac{FeO_t \text{ wt.}\%}{71.85} \right)} \quad [2]$$

= 53.95 (< 68–75 for primary magmas) for the representative amphibolite sample A1.

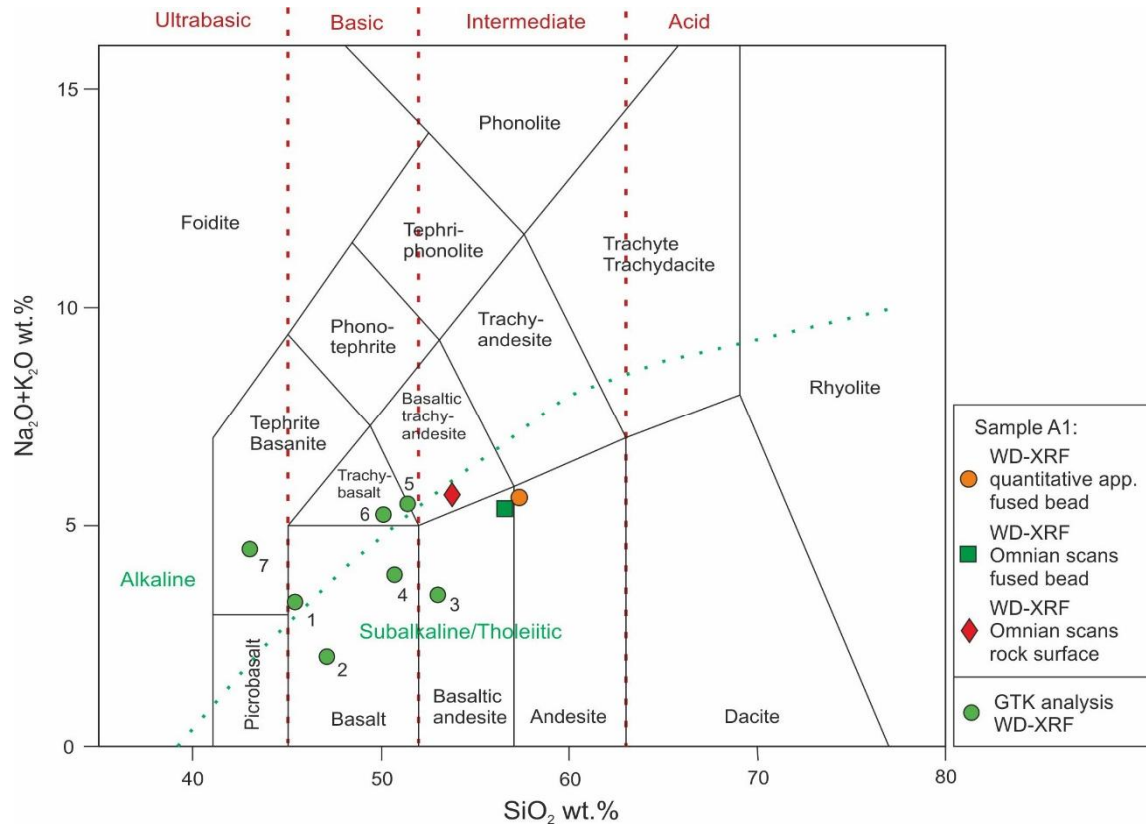


Figure 9. Results of three different WD-XRF analyses conducted for amphibolite sample A1 plotted in TAS diagram. Quantitative method sets the composition to the andesite field, close to basaltic andesite field. Selected values from GTK rock geochemical database of Finland of temporally related amphibolite units for reference (Fig. 16 and Appendix VII). Redrawn from Le Bas et al. (1986).

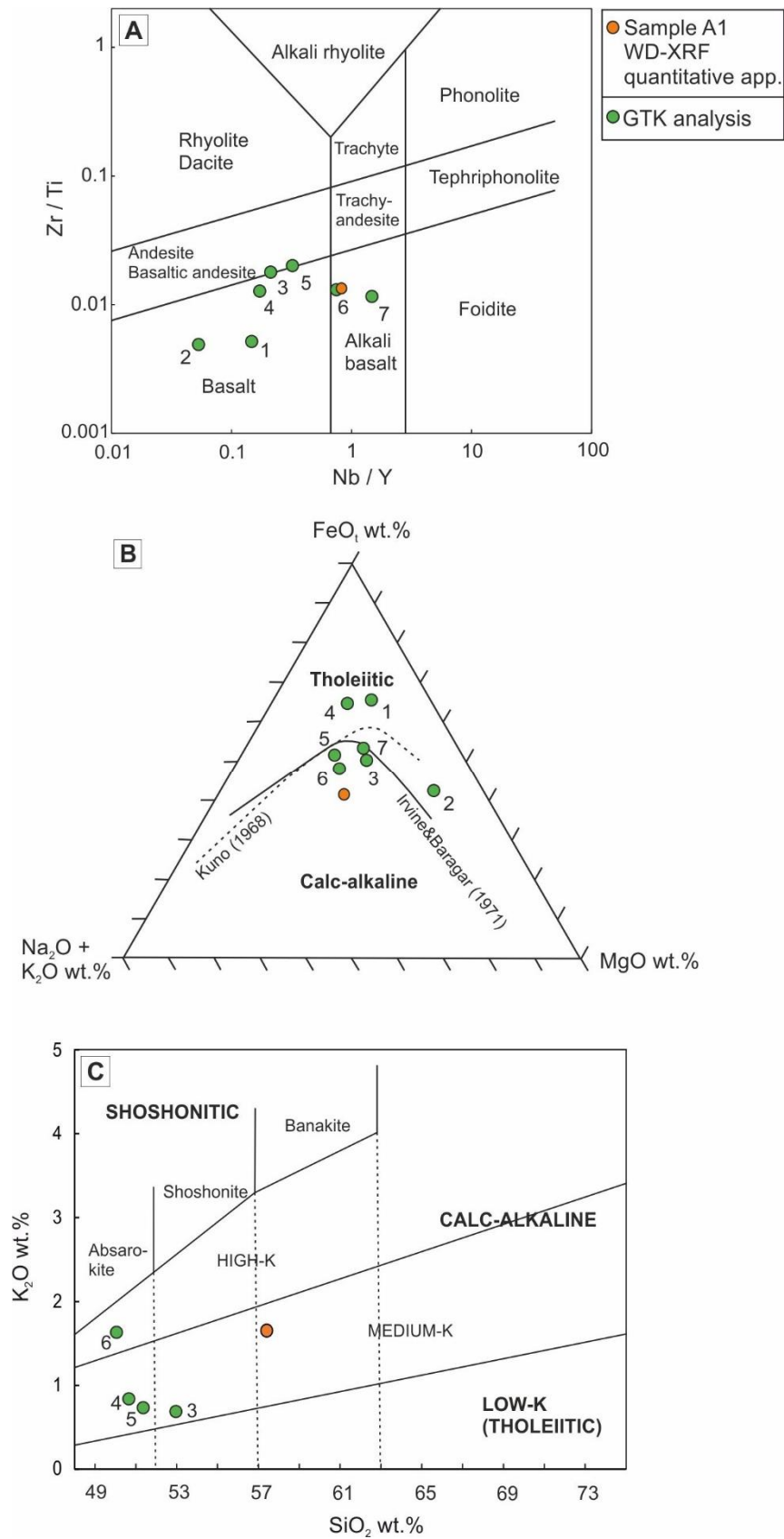


Figure 10 A: WD-XRF quantitative result falls in alkali basalt field in Zr/Ti v. Nb/Y diagram. Redrawn from Pearce (1996; revised from Winchester & Floyd 1977). B and C: Quantitative WD-XRF result plotted on AFM diagram and K-field diagram (redrawn from Ewart 1982), both indicating calc-alkaline series. Selected values from GTK rock geochemical database of Finland of temporally related amphibolite units for reference (Fig. 16 and Appendix VII).

6.2 Comparison of the XRF methods

6.2.1 Amphibolite sample A1

The amphibolite sample A1 was used to compare and evaluate the different XRF analysis methods (Table 3). It seems that values gained from fused bead especially in terms of major element oxides are quite similar whether they were obtained with Omnian scans or quantitative application (Table 3, Fig. 11).

Table 3. Whole-rock chemical composition of amphibolite sample A1 obtained with different XRF methods. All results of the ten P-XRF analyses are tabulated in Appendix I.

Method	WD-XRF quantitative fused bead	WD-XRF Omnian scans fused bead	WD-XRF Omnian scans rock surface	P-XRF* mining mode rock surface
n	1	1	1	10
SiO ₂ (wt. %)	57.41	56.60	53.97	57.94
TiO ₂	0.97	0.95	0.85	0.80
Al ₂ O ₃	15.37	15.55	15.76	10.93
FeOt	7.50	7.69	5.72	6.19
MnO	0.12	0.13	0.11	0.12
MgO	4.93	4.91	3.69	1.71
CaO	6.06	5.87	5.68	6.32
Na ₂ O	3.93	3.69	4.17	n.a.
K ₂ O	1.65	1.68	1.50	1.19
P ₂ O ₅	0.19	0.20	0.21	0.18
Sum	98.13	97.27	91.65	85.37
Ba (ppm)	415	360	340	520
Cl	n.a.	n.d.	670	210 ⁷
S	n.a.	70	100	220 ⁸
Ce	48	n.d.	n.d.	n.a.
Cr	154	240	120	240
Cu	8	n.d.	n.d.	n.d.
La	19	n.d.	n.d.	n.a.
Nb	14	n.d.	10	n.d.
Ni	23	230	60	60 ²
Rb	72	150	40	20
Sn	n.a.	n.d.	n.d.	40 ²
Sr	292	350	320	230
U	4	n.d.	n.d.	n.a.
V	157	190	120	240
Y	17	n.d.	10	n.a.
Zn	65	n.d.	40	n.a.
Zr	78	110	90	70

*= P-XRF results are averages of ten sawed surface analyses.

Superscripted numbers indicate the number of values included in the average value if all are not included.

n= number of analyses

n.a.= not analyzed

n.d.= not detected

Comparing the Omnian scans results suggests, that changing the sample type from fused bead to sawed rock surface, has a notable negative effect on the results. Major oxide sum value drops from 97.27 wt.% to 91.65 wt.%. Most of the major element oxide values are lower than the ones obtained with Omnian scans on fused bead or quantitative application. Oxide values that are higher in Omnian rock surface results are Al_2O_3 with 15.76 wt.%, Na_2O with 4.17 wt.% and P_2O_5 with 0.21 wt.%. The effect of changing from fused bead to rock surface is visible in Figure 11, where Omnian scans and quantitative application results from fused bead do not differ remarkably, but Omnian scans results from rock surface are clearly different from these two.

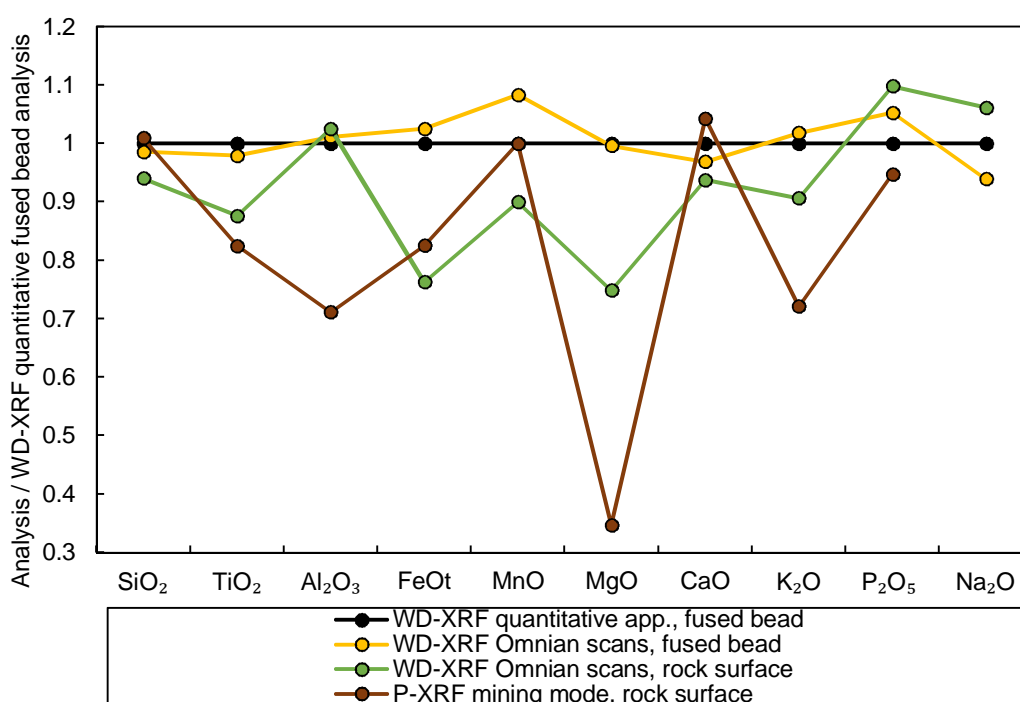


Fig 11. Amphibolite sample A1 XRF results of major element oxides as ratios compared to quantitative application results. P-XRF results are averages of ten sawed surface analyses and do not include Na_2O . All results of the ten P-XRF analyses are tabulated in Appendix I.

P-XRF major oxide values are notably lower on average than values obtained with WD-XRF quantitative application or Omnian scans from fused bead, SiO_2 (57.94 wt%), MnO (0.12 wt.%), CaO (6.32 wt%) and P_2O_5 (0.18 wt.%) being the exceptions. MgO value (1.71 wt.%) is undoubtedly too low and not reflecting the real rock composition.

Taking a closer look on the ten individual P-XRF sawed surface values and comparing them to WD-XRF quantitative application values (Fig. 12), it is revealed how

amphibolite sample heterogeneity scatters the P-XRF results. Comparison to quantitative application also shows which major element oxide values are altogether, heterogeneity considered, erroneous in P-XRF results.

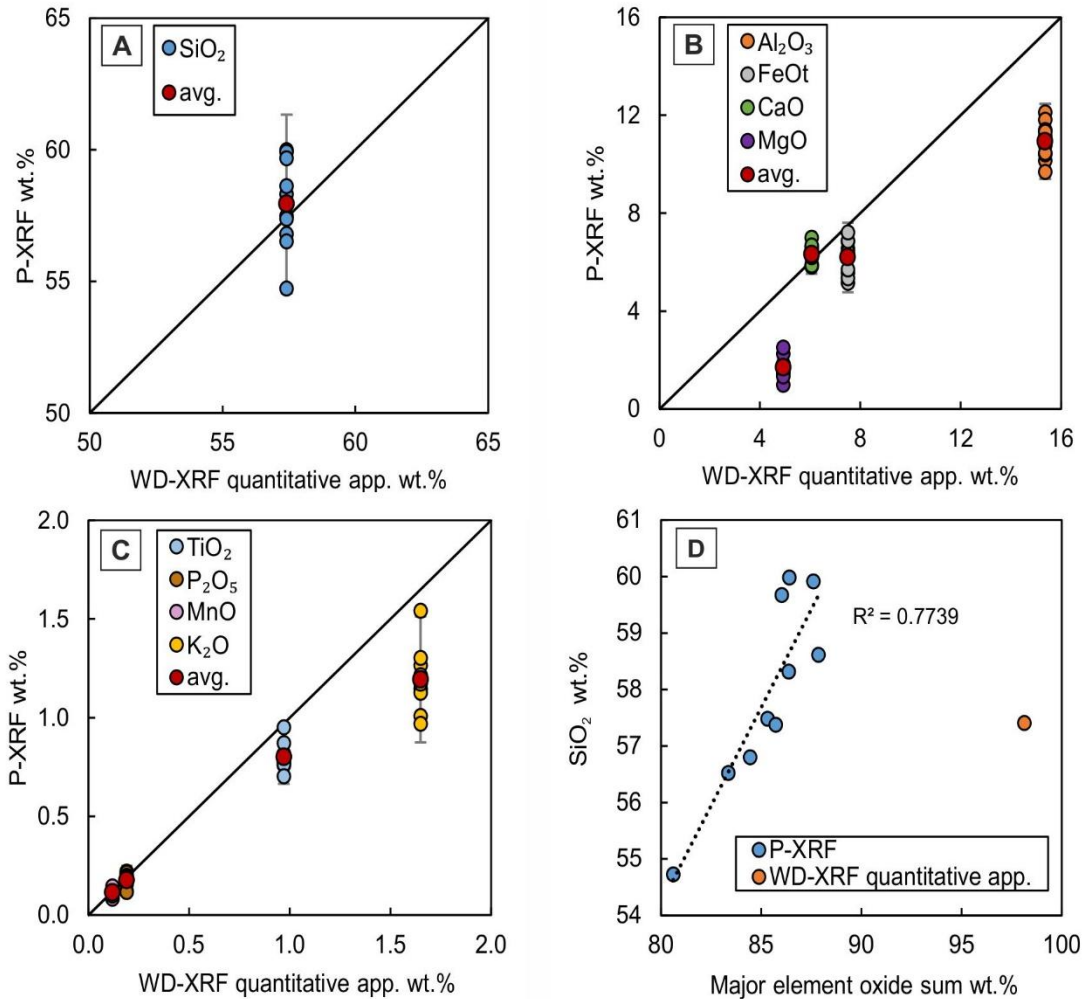


Figure 12. A, B and C: Ten P-XRF results of the sawed surface of amphibolite sample A1 compared to quantitative application values of the fused bead. Major element oxides are divided in three diagrams depending on their weight percent range. 2 x standard deviation (2σ) bars and average values are included. D: P-XRF SiO₂ wt.% values correlation to major element oxide sum wt.% values, with R squared value of 0.7739 indicating relatively high correlation.

Tabulated results of the ten P-XRF analyses, both on sawed and curved rock surfaces can be seen in Appendix I and II. Values in Fig. 12 are untreated; thus, the sum of major element oxides is not constant between the methods. Correlation between P-XRF SiO₂ values (that range between 54.73–59.98 wt.%) and major element oxide sum values (80.61–87.86 wt.%) is clearly visible, with R squared value of about 0.77. Quantitative application SiO₂ value is 57.41 wt.% with major element oxide sum value of 98.13

wt.%. This observation suggests that if the P-XRF oxide sum would hypothetically be 100 wt.%, SiO₂ would probably be overrepresented in P-XRF results. However, the average of P-XRF SiO₂ values is very close to quantitative value (Fig. 12.A), which is a quite promising result for P-XRF device.

P-XRF values of Al₂O₃ (range between 9.69–12.12 wt.%), MgO (0.99–2.52 wt.%) and K₂O (0.97–1.54 wt.%) values are all clearly lower than quantitative application values (15.37 wt.%, 4.93 wt% and 1.65 wt% respectively). FeO_t (5.15–7.21 wt.%) and TiO₂ (0.70–0.95 wt.%) are just slightly lower than quantitative application values (7.50 wt.% and 0.97 wt.% respectively).

6.2.2 Sawed amphibolite pieces: P-XRF and Omnian scans comparison

Widening the comparison from sample A1 to twelve sawed amphibolite pieces from different depths (3.90, 36.00, 63.35, 88.95, 105.35, 128.30, 156.00, 203.00, 241.55, 323.20, 336.70 and 361.60 m, Fig. 2) of the core, the heterogeneity of the amphibolite can be studied on a wider scale. All major element oxide values seem to be scattered (Fig. 13, notice the scales) with both methods. Presented values are once again untreated so major element oxide sum is not constant between the methods. Major element oxide sums vary between 84.37–90.72 wt.%, averaging at 88.11 wt.% with P-XRF device and between 89.29–94.42 wt.%, averaging at 92.29 wt.% with Omnian scans (Appendix III and IV).

SiO₂ values, that are scattered between 54.13–64.51 wt.% with P-XRF, are all higher than corresponding Omnian scans values (48.22–59.32 wt.%), whereas Al₂O₃ (varying between 11.04–14.01 wt.%) and MgO (0.53–2.61 wt.%) with P-XRF are all higher with Omnian scans (14.89–18.07 wt% Al₂O₃ and 3.36–7.45 wt.% MgO) (Fig. 13 and Fig. 14). Especially in the case of MgO, the range is wider in Omnian scans than P-XRF. CaO results seem to correlate quite well and K₂O is rather close to 1:1 correlation as well. Other oxide results are scattered without a clear trend.

Omnian scans method and P-XRF were previously observed to give values for rock surface that are on average lower than quantitative method results of fused bead (Fig. 11). Major relations between P-XRF and Omnian scans from rock surface shown in Fig.

11 (e.g. MgO and Al_2O_3 ratios) are clear in twelve sample comparisons as well, but all differences between the methods are clearly not constant.

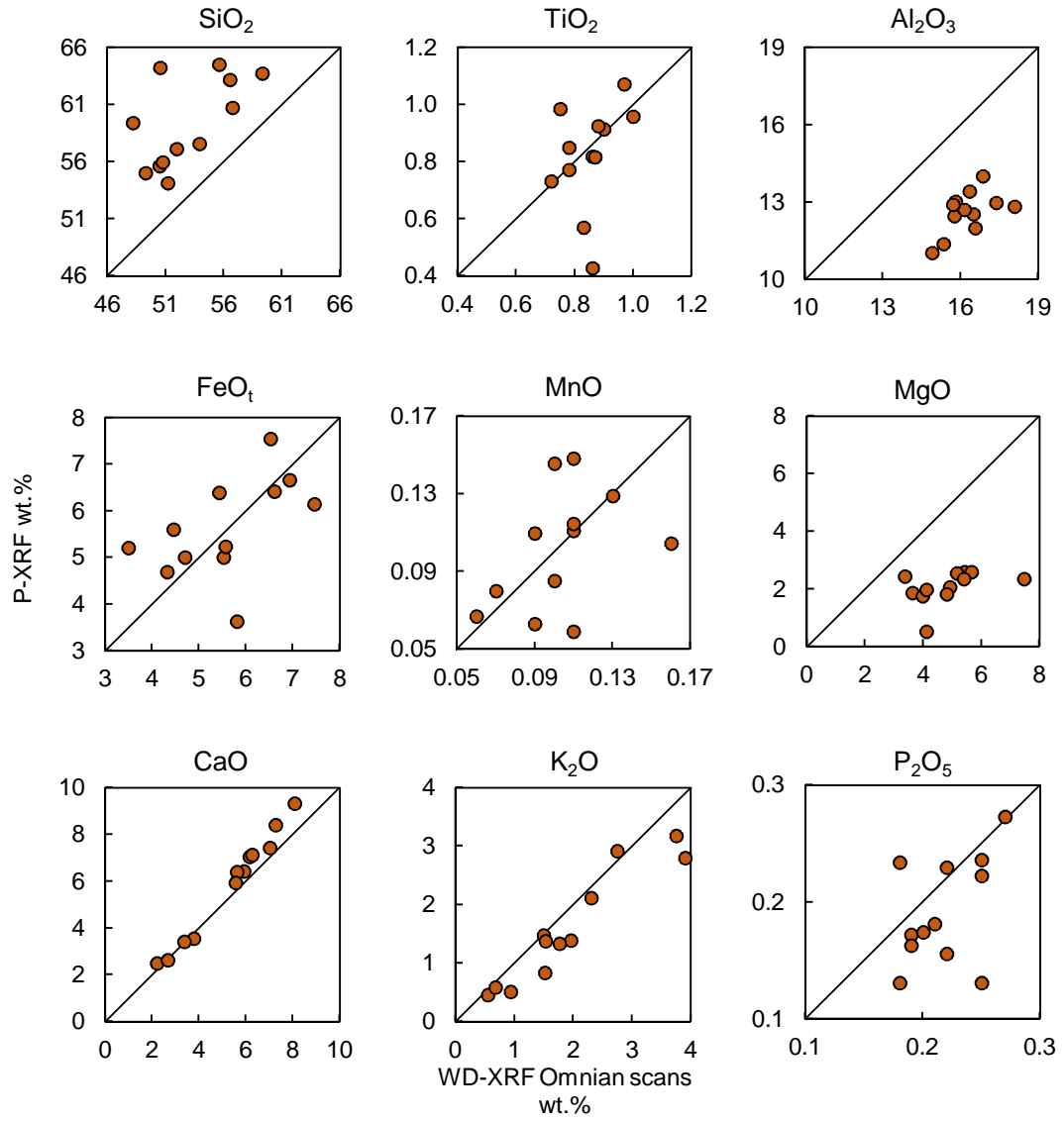


Figure 13. P-XRF and Omnian scans results of the twelve amphibolite samples. Black line from lower left corner to upper right corner represents 1:1 correlation between the methods. Na_2O is excluded.

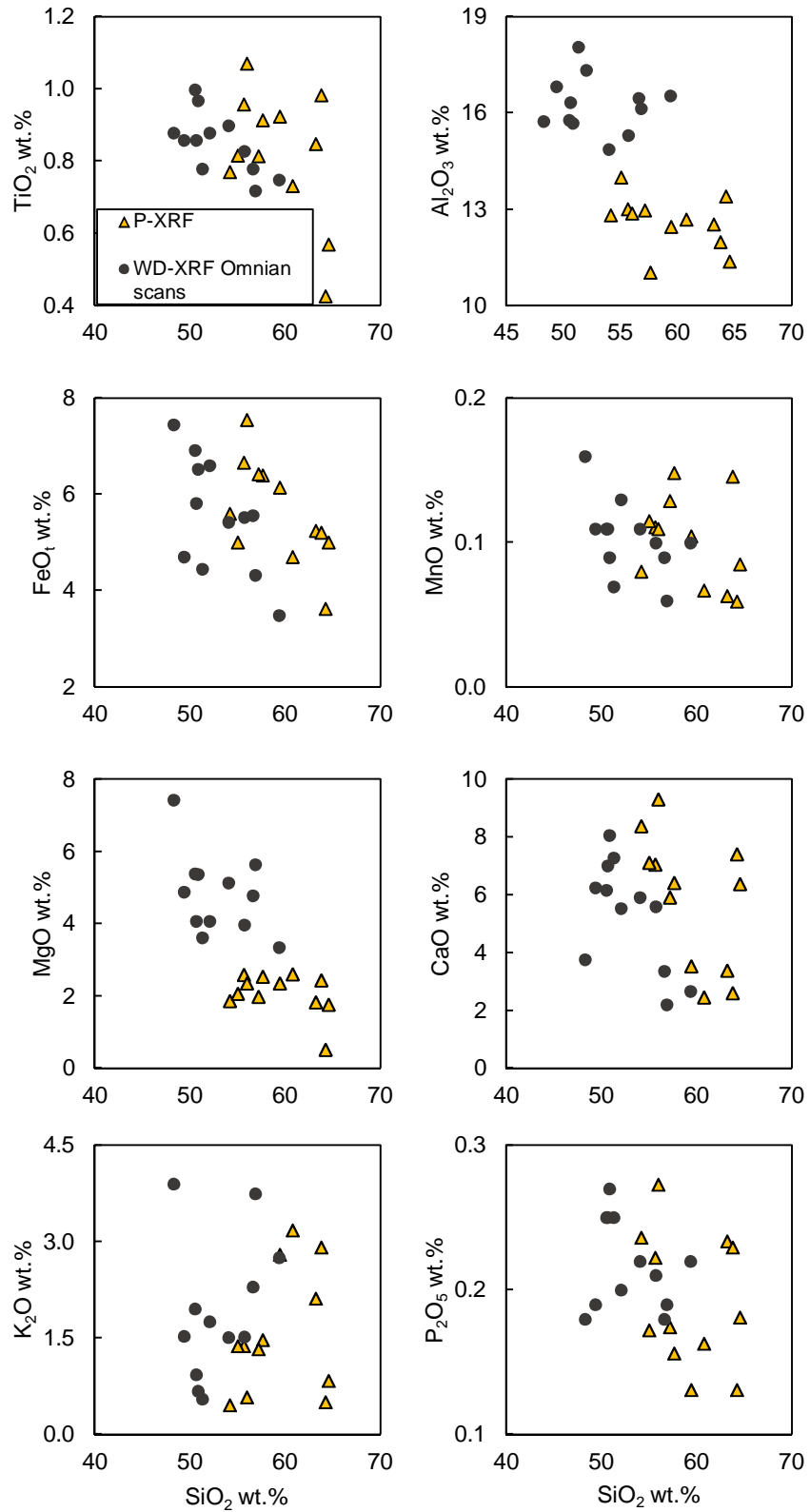


Figure 14. Harker diagrams of P-XRF and WD-XRF Omnian scans values for the twelve amphibolite samples.

6.3 Whole drill core analysis with the P-XRF device

To evaluate the feasibility of P-XRF during drill core logging, the curvature of the core was first considered. In addition to ten repeated P-XRF analyses of the sawed surface of amphibolite sample A1, curved core surface of the same piece was also analyzed repeatedly.

Compared to the sawed surface results (Fig. 15), curved surface values seem to have a bit wider range, with average values of e.g. SiO_2 (57.14 wt.%), TiO_2 (0.90 wt.%) and K_2O (1.45 wt.%) (Appendix I and II) that are even closer to quantitative application values than sawed surface P-XRF values (57.94 wt.%, 0.80 wt.% and 1.19 wt.% respectively). Sawed surface has major element sum values varying between 80.61 wt.% and 87.86 wt.% averaging at 85.37 wt.% and curved surface between 80.08 wt.% and 89.26 averaging at 84.63 wt.%. Differences in the values between the surfaces are however relatively minor in general.

Major element oxide sum values for the whole length of the core range between 74.70 wt.% and 92.63 wt.%, averaging at 84.00 wt.%. Main element oxide sums and other tabulated P-XRF results for the whole length of the core can be seen in Appendix V.

Comparing the selected oxides P-XRF results to depth and lithology (Fig. 16), variation in major element oxide values between different rock types can be observed. Changes in SiO_2 content alone clearly indicate changes from mafic amphibolitic and actinolite-rock units to felsic granitoid units. Between 170 m and 220 m, SiO_2 and Al_2O_3 values seem quite constant but FeO_t values show relatively high variation. Relatively high FeO_t and CaO values of actinolite rock (Table 2) is visible between 250–300 m with quite thin actinolite rock sections.

Although relative variation in major element oxide values can be observed between the rock types, possible changes in the geochemistry of the amphibolite along the length of the drill core is not distinguished. Omnian scans values of twelve amphibolite pieces do not seem to correlate with depth either, but higher values of Al_2O_3 compared to P-XRF is once again observed (Fig. 16).

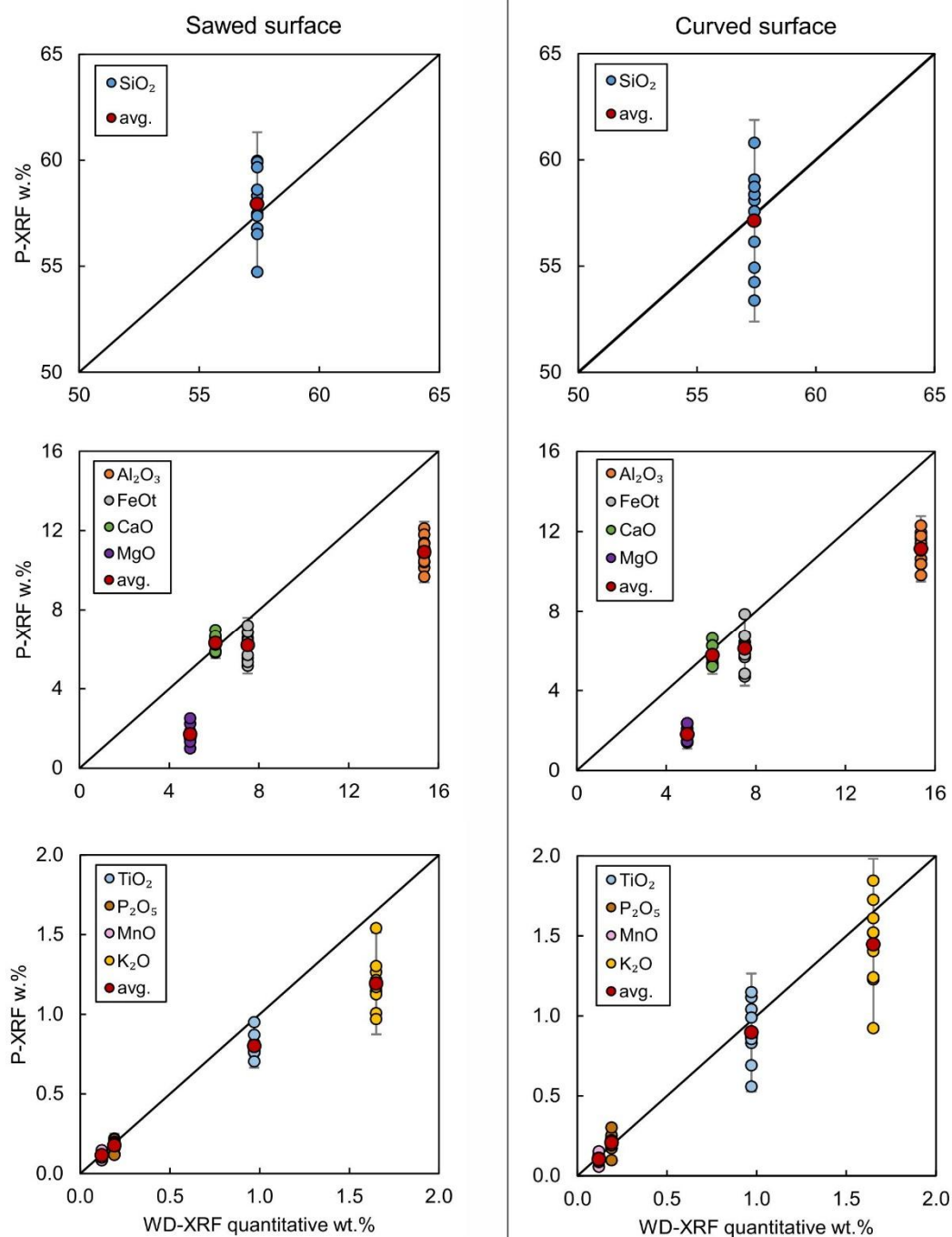


Figure 15. Ten P-XRF analyses of sawed and curved drill core surfaces of the amphibolite sample A1 compared to quantitative WD-XRF values.

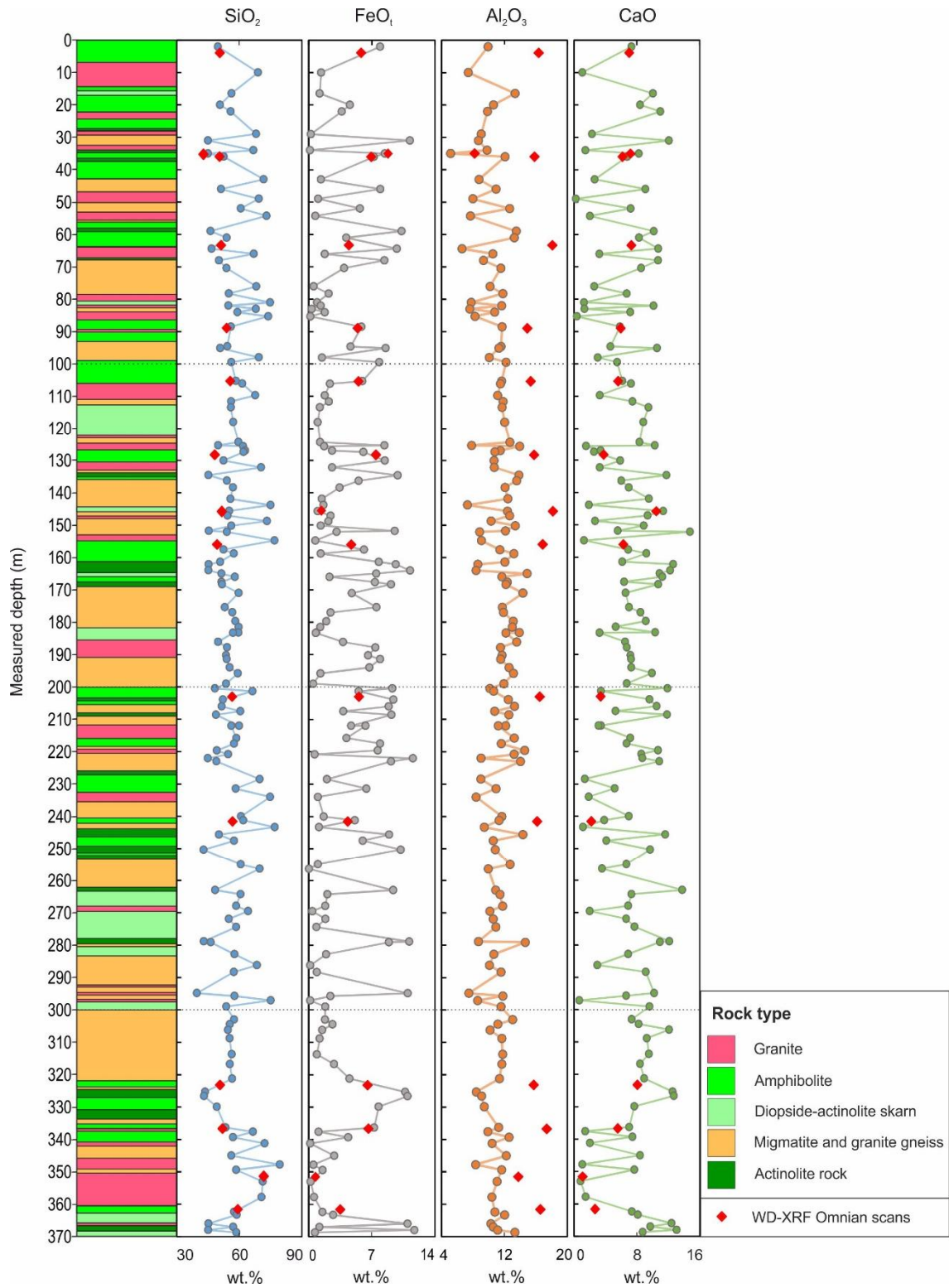


Figure 16. Rock types and P-XRF values of selected major element oxides compared to depth. Omnian scan values of twelve amphibolite samples and granite, actinolite rock and diopside-actinolite skarn are marked as red spots. Variation in geochemistry can clearly be observed between the rock types.

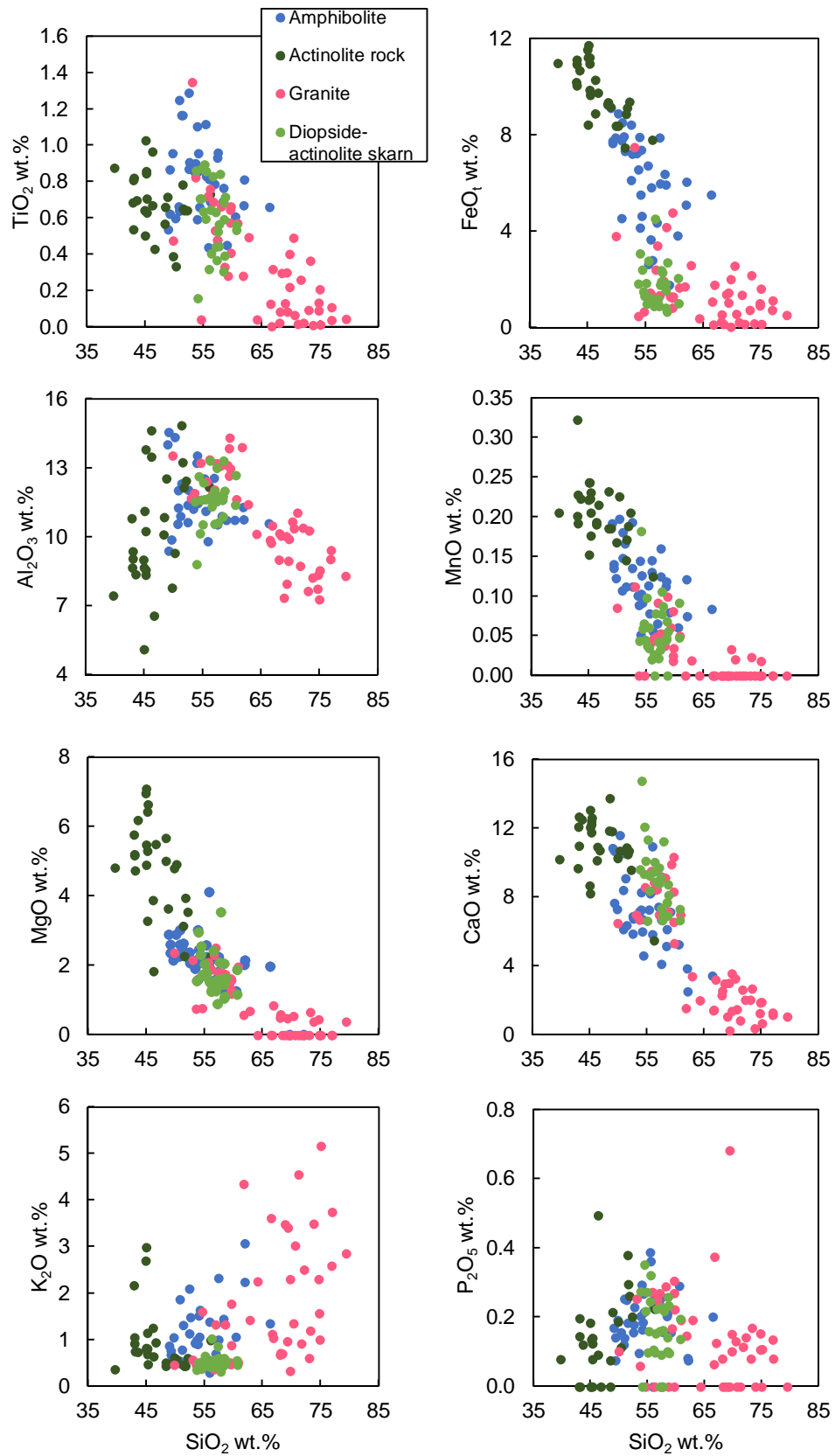


Figure 17. Harker diagrams of all P-XRF results of the drill core color coded by initially determined rock types.

Illustrating the P-XRF core results according to initially determined rock type classes (Fig. 17), major element oxide results show some trends and groups. Comparing to SiO_2 wt.% values in Harker diagrams, TiO_2 , FeO_t , MnO , MgO and CaO wt.% clearly decrease as SiO_2 wt.% increase. K_2O and P_2O_5 do not seem to show any trends, but some value ranges are favored over others. Al_2O_3 is the only major element oxide that seems to have completely different trendline depending on rock type: actinolite rock has positive trend and granite negative, changing at about 55 wt.% SiO_2 , which is possibly caused by the fractioning of feldspars.

Indeed, broad classes of different rock types can be distinguished from the P-XRF results alone without visual examination or previous lithological logging, especially from FeO_t , SiO_2 , MgO and MnO results. Some ranges for major element oxides can also be derived from the results, although P-XRF results cannot be considered quantitative. Comparisons between quantitative WD-XRF values and P-XRF values of sample A1 (Fig. 15) clarify that untreated P-XRF results from the rock surface concerning for example SiO_2 , CaO and MnO are quite close to the most accurate quantitative application results. The accuracy of the P-XRF results needs to be considered when examining the results of the whole drill core. Additional consideration is needed with major element sum values that are not very high (84.00 wt.% on average).

6.4 Outcrops: effects of surface quality and field circumstances

In the case of outcrops, quality of the analysis surface became highly important factor for the analysis to be successful, since no sample preparation was done. Outcrops were varyingly rough, weathered, altered and usually covered in e.g. lichen, moss and pollution, which seemed to dramatically affect the detection of underlying bulk rock elements. These surfaces are later called “poor quality surfaces”. “Good quality surfaces” are grouped as being as clean as possible, considering the circumstances, but weathering and roughness could not be completely avoided. Results of the outcrop analyses show variation in success of the analyses from outcrop to another (Appendix VI) and from good quality surface to poor quality surface (Table 4).

Table 4. Geochemical comparison of good quality and poor quality amphibolite outcrop surfaces. Results obtained with P-XRF.

	Good quality surface	Poor quality surface
n	47	45
SiO ₂ (wt.%)	49.79	25.34
TiO ₂	0.73	0.42
Al ₂ O ₃	7.91	3.40
FeO _t	3.37	3.45
MnO	0.06 ³⁸	0.05 ³⁵
MgO	0.95 ⁴³	0.20 ¹⁰
CaO	4.50	2.51
K ₂ O	1.10	1.44
P ₂ O ₅	0.23 ⁴⁵	0.58
Total	68.64	37.39
Ba (ppm)	370	410
Cl	130 ⁹	520 ³⁸
S	1300 ⁴⁵	5950
Co	n.d.	180 ²
Cr	170 ⁴⁶	180
Cu	60 ¹	50 ¹⁶
Ni	210 ¹	130 ²
Pb	30 ³⁰	50 ³⁸
Rb	40 ¹⁶	30 ²⁴
Sn	40 ³	40 ²
Sr	190	170
V	170 ⁴⁴	150 ⁴²
W	100 ¹	90 ²
Zn	50 ³⁸	100
Zr	100	90

n = number of analyses

n.d.= not detected

Superscripted numbers indicate the number of values included in the avg. value if all are not included

Distinguishing different rock types was challenging from weathered and covered surfaces. Therefore, the amphibolite average values presented in Table 4 are probably of compositionally more variable amphibolite than in the drill core. Major element oxide sum of amphibolite from all outcrop analyses (good + poor surfaces) is only 53.35 wt.% on average (Table 5). Major oxide sum value is notably low on average regardless of whether the surfaces were clean or not (Table 4), yet poor quality surfaces have an average oxide sum value of almost half of that of the good quality surfaces.

Although having very low major oxide sum values, poor quality surface results show remarkably high amounts of P₂O₅ (0.58 wt.%), S (5950 ppm) and Cl (520 ppm) compared to clean surface results (0.23 wt.%, 1300 ppm and 130 ppm respectively). Also, FeO_t (3.45 wt.%), K₂O (1.44 wt.%), Ba (410 ppm), Cr (180 ppm) Pb (50 ppm), and Zn (100 ppm) are higher on covered surfaces. Good quality surface results are 3.37 wt.%, 1.10 wt.%, 370 ppm, 170 ppm, 30 ppm and 50 ppm respectively. Poor detection of light elements is visible in outcrop results as well with 0.95 wt.% MgO and 7.91 wt.% Al₂O₃ values for good quality surfaces on average. Cu was detected more likely from poor quality surfaces (Table 4).

Table 5. All amphibolite results and average results obtained with different XRF methods.

Sample type	Core							Outcrops
	Piece A1				Sawed pieces		Core surface	Rock surface
	n	1	1	10	12	12	38	92
Method	WD-XRF quantitative fused bead	WD-XRF Omnian scans fused bead	WD-XRF Omnian scans rock surface	P-XRF* mining mode sawed rock surface	WD-XRF* Omnian scans rock surface	P-XRF* mining mode rock surface	P-XRF* mining mode rock surface	P-XRF* mining mode rock surface
SiO ₂ (wt.%)	57.41	56.60	53.97	57.94	52.90	59.26	55.63	37.83
TiO ₂	0.97	0.95	0.85	0.80	0.85	0.82	0.78	0.58
Al ₂ O ₃	15.37	15.55	15.76	10.93	16.27	12.61	11.56	5.70
FeO _t	7.50	7.69	5.72	6.19	5.57	5.64	5.82	3.41
MnO	0.12	0.13	0.11	0.12	0.10	0.10	0.11	0.05 ⁷³
MgO	4.93	4.91	3.69	1.71	4.82	2.08	2.12	0.58 ⁵³
CaO	6.06	5.87	5.68	6.32	5.34	5.84	6.86	3.53
Na ₂ O	3.93	3.69	4.17	n.a.	4.28	n.a.	n.a.	n.a.
K ₂ O	1.65	1.68	1.50	1.19	1.93	1.57	1.18	1.27
P ₂ O ₅	0.19	0.20	0.21	0.18	0.22	0.19	0.19	0.40 ⁹⁰
Sum	98.13	97.27	91.65	85.37	92.28	88.11	84.25	53.35
Ba (ppm)	415	360	340	520	250	410	430	390
Cl	n.a.	n.d.	670	210 ⁷	180	130 ²	130 ³	450 ⁴⁷
S	n.a.	70	100	220 ⁸	150	760 ⁶	420 ³¹	3630 ⁹⁰
Ag	n.a.	n.d.	n.d.	n.d.	n.d.	100	n.d.	n.d.
Bi	n.a.	n.d.	n.d.	n.d.	n.d.	10 ²	n.d.	n.d.
Ce	48	n.d.	n.d.	n.a.	n.d.	n.a.	n.a.	n.a.
Co	n.a.	n.d.	n.d.	n.d.	60 ¹	n.d.	n.d.	180 ²
Cr	154	240	120	240	200	290	280	170 ⁹¹
Cu	8	n.d.	n.d.	n.d.	30 ¹¹	60 ¹	110 ⁵	50 ¹⁷
F	n.a.	n.d.	n.d.	n.a.	1620 ⁷	n.a.	n.a.	n.a.
Ga	n.a.	n.d.	n.d.	n.a.	20	n.a.	n.a.	n.a.
La	19	n.d.	n.d.	n.a.	n.d.	n.a.	n.a.	n.a.
Nb	14	n.d.	10	n.d.	10	10	n.d.	n.d.
Ni	23	230	60	60 ²	60	60 ²	80 ⁵	n.d.
Pb	n.a.	n.d.	n.d.	n.d.	20 ⁸	10	20 ¹¹	40 ⁶⁸
Rb	72	150	40	20	100	50 ¹⁰	30 ²⁴	35 ⁴⁰
Sn	n.a.	n.d.	n.d.	40 ²	n.d.	30 ⁴	40 ⁴	40 ⁵
Sr	292	350	320	230	300	220	220	180
U	4	n.d.	n.d.	n.a.	n.d.	n.a.	n.a.	n.a.
V	157	190	120	240	190	250	260	160 ⁸⁶
W	n.a.	n.d.	n.d.	n.d.	n.d.	60 ²	n.d.	90 ³
Y	17	n.d.	10	n.a.	20 ¹	n.a.	n.a.	n.a.
Zn	65	n.d.	40	n.a.	70	50	50 ³⁶	70 ⁸³
Zr	78	110	90	70	110	60	70	100

*= Results are averages, superscripted numbers indicate the number of values included in the avg. value if all are not included

n= number of analyses

n.a.= not analyzed

n.d.= not detected

7. DISCUSSION

7.1 Error and contamination sources of the analyses

7.1.1 Sample preparation

For the XRF results to actually represent the source rock composition, especially unprepared samples need to be selected with care and keeping the requirements of the analysis surface diameters of the devices in mind. The round detection area of P-XRF is only 8 mm in diameter and that of WD-XRF 27 mm, which limits the representativeness of the results, especially in the case of coarse-grained samples. When analyzing with P-XRF without any sample preparation, rock types with smaller grainsize probably give more exact results of the geochemistry than rock types that are coarser. Coarseness of the rock type can be compensated by taking multiple analyses of the sample from different spots, so every mineral is definitely represented in the average results.

Aforementioned problems related with heterogeneity are minimized by preparing a fused bead with highly homogeneous composition. However, multiple stages of the preparation increase the possibility of contamination. In this work, unknown contamination starts in the drilling process with possible contamination from the diamond drill and initial handling of the core. Possible contamination on sample surface can be avoided, when picking the fragments for melting of fused bead, but when analyzing the core surface directly with P-XRF device, detecting the possible surface contamination is unavoidable.

During the powdering of picked fragments of sample A1, the most notable contamination sources were the tungsten carbide pan, the bullets and the Co binder. In the melting process, the Pt-Au alloy crucible and Li, B and Br of the fluxing agent were sources of contamination. Any kind of skin contact with the sample during the whole preparation was avoided for minimizing the skin contamination of e.g. K, Cl and S (Worley et al. 2006). Even thicknesses of the prepared samples for surface analyses and smoothness of the sample surfaces were also paid attention to, because of possible

effect later in analysis on the intensity of the emitted fluorescence (Potts et al. 1997a, Marguí 2013).

7.1.2 Analysis

The error sources related to the analysis process can be examined in two groups: instrumental errors and errors caused by the sample composition, known as matrix effects.

XRF spectrometers produce characteristic X-rays from Be-window and Rh-anode (in WD-XRF device) or Ag-anode (in P-XRF device) of the X-ray tube, which can be minimized by placing different filters between the tube and the sample (e.g. Potts and Webb 1992). Fluorescence might also be emitted from analyzing crystal and detector gas of WD-XRF device (Marguí 2013). Major problems with the energy dispersive detection style of P-XRF are related to the reduced resolution compared to WD-XRF (Young et al. 2016). Adding the miniaturized technology of a portable size, the detection of light elements become difficult (e.g. Mg and Al) or impossible (Na and lighter). In general, the detection limits are higher than with WD-XRF. The power of the X-ray tube of the portable device is clearly lower than that of laboratory apparatus and the rechargeable batteries slowly run down during long analysis series. This might negatively affect the success of P-XRF analyses.

In the sample itself, matrix effects are the biggest challenge. This means that other elements cause a distraction in the analysis process. In the energy spectrum, the neighboring elements might absorb or enhance each other, which is a problem in a sample with great compositional variability such as geological samples (Norrish and Hutton 1968). In WD-XRF analysis, the relatively good resolution decreases the elemental peak overlaps in the spectrum (Marguí 2013).

In addition to characteristic fluorescence of an element, secondary and even tertiary fluorescence, that all pile up in the results, are excited in the sample and detected. Also, Auger-emission, Compton scattering and Rayleigh scattering are caused by the incoming X-ray beam in the sample. Multiple correction methods such as FP in WD-XRF automatically correct previously mentioned error sources (Marguí 2013).

Quantitative correction might be done by the user with WD-XRF Omnian scans with manually modifying the Omnian spectrums, which can be considered as an error source as well.

7.1.3 Outcrop notes

When working in field and analyzing outcrops without sample preparation, the surface features become highly important factors affecting the success of the analyses. The reasons for notable amounts of e.g. Cl, P and especially S in the outcrop analyses (Table 4) are beyond the range of this work, but it can be concluded that different kinds of coverings are to be taken into account when working in field.

In addition to coverings and weathering, surface smoothness and grain size affect the outcrop analyses. Hardly ever is the outcrop so smooth that P-XRF device can be pressed tightly against the rock during the analysis. Uneven surface makes it harder for the emitted X-rays to “hit the target” and they might escape during the analysis (Potts et al. 1997b). Also, all the fluorescence might not get detected when there is space between the sample and the apparatus (Potts et al. 1997b). Curviness of the drill core surface causes the same problem although surface is smooth. Many error sources mentioned above can be eliminated or at least minimized with the attentiveness of the user, which is a remarkable part of working with P-XRF.

7.2 Feasibility of the introduced methods in field and drill core analyses

Table 6 summarizes the major differences regarding the use of the introduced methods. Whether conducting outcrop or drill core analyses, required quality of the results usually direct the decision when choosing between the methods available. Both qualitative and quantitative results are obtained only with WD-XRF quantitative application that utilizes calibrations with certified reference materials. WD-XRF Omnian scans reach to the level of being semi-quantitative and the actions of the user are in important role when evaluating the results. Good quality results are obtained with Omnian scans especially when fused bead is used as a sample type. Changing the sample type to rock surface has a remarkable effect on the results and quantitiveness

of the method decreases (Table 3, Fig. 11). Instrumental complexity increases the resolution of WD-XRF making it more quantitative but challenging to fit in a portable model.

P-XRF is as well semi-quantitative at the most. As suggested before (Fig. 12), depending on the element, P-XRF can give on average quite accurate results, e.g. for SiO_2 at least in the case of amphibolite. The relatively low price when compared to complex laboratory apparatus lowers the bar for choosing P-XRF as the method for at least preliminary analysis. P-XRF cannot replace accurate, quantitative methods, but in cases when sample cannot be detached, destroyed or modified, P-XRF might be the best choice also in semi-quantitative laboratory analyses. Therefore, when the most accurate whole rock geochemical results are not required, but broad classification is the target, Omnian scans for the sawed pieces of the core might not give significant further information compared to P-XRF, which might be considered more cost-effective method to obtain the wanted information.

Detecting hazardous substances in soils, sediments and pre-concentrated waters, or doing other scientific research, where collecting samples is restricted, semi-quantitative *in situ* analyses conductible with P-XRF spectrometer will absolutely be beneficial. Especially in field circumstances the fastness and ease of use are desirable properties. Holding the device in hand provides flexibility for indoor analyses also when for example drill core does not need to be removed from its container.

However, if quantitative results are required, the sample needs more preparation which is time-consuming and thus underlines the importance of careful selection of the most representative sample. Choosing the Omnian scans application for WD-XRF analysis, instead of WD-XRF quantitative application, stretches the sample type requirement. Time-consuming sample preparation of fused bead or pressed powder pellet can be skipped, if wanted, and a representative solid rock piece can be analyzed instead. However, chipped sample from an outcrop with altered or covered surface probably needs more preparation than drill core sample that may also already have the correct diameter to fit in the sample holder of the WD-XRF spectrometer. Polishing the analysis surfaces of the samples would easily eliminate any error sources related to surface topography.

In consequence, depending on the chosen method, preparation or lack of preparation cause multiple points of consideration for the evaluation of the results: representativeness, heterogeneity and contamination. User is also in an active role in every XRF method, whether during the sample preparation (WD-XRF) and/or during the analysis itself (P-XRF) or in correcting the received spectrums (WD-XRF Omnian scans). Utilizing portable XRF device does not require expertise and the procedure is quite straightforward. Yet, handheld device requires much more attention from the user during the analysis for the analyses to be successful than laboratory devices. On the other hand, laboratory WD-XRF devices require expertise during the whole analysis process from sample preparation to results evaluation. The professionalism of the user need to be taken into account in the evaluation of error sources and contamination.

Table 6. Main differences regarding the use of XRF methods introduced in this work.

Method	Axios mAX WD-XRF quantitative app.	Axios mAX WD-XRF Omnian scans	Niton XL3t GOLDD+ portable ED-XRF mining mode
Data quality	qualitative + quantitative	qualitative+ semi-quantitative	qualitative+ semi-quantitative
Detectible elemental range	O–U	O–U	Mg–U
Sample type	fused bead	fused bead powder pellet solid rock surface	almost any kind
Contamination from	sample prep.	sample prep.	sample prep. coverings in outcrops
Error sources	matrix effects instrumental errors	matrix effects instrumental errors heterogeneity surface topography spectrum modification	matrix effects instrumental errors heterogeneity surface topography
User activity	sample prep. application options	sample prep. spectrum modification	holding the apparatus
Expensiveness of the device (to purchase and maintain)	relatively expensive	relatively expensive	relatively inexpensive
Required expertise	high	high	low
Fastness	relatively slow	relatively slow	relatively fast

7.3 Improvements and possible future studies regarding the P-XRF

The effect of weathering and contamination on the analysis surfaces of the outcrops was not studied very extensively in this work. The major conclusions were that the major element oxide sums were on average notably lower compared to drill core results. Although clean surfaces can be favored over the covered ones in field, the surfaces are always uneven which has a huge impact on the success of the analysis. In addition to unevenness, different coverings have a remarkable effect on the results. For example S, Cl and P are more abundant on the outcrop surfaces for unknown reasons. It would require more examining and expertise of different scientific fields to reveal the effects of different coverings.

Potts et al. (2006) examined the weathering effects on the P-XRF results and based on surface concentrations and bulk rock compositions calculated ratios for correcting the weathering effects for different elements in rhyolite and dolerite samples. Corrected values were compared to accurate WD-XRF results of the rocks and corrections were found to improve some element values and worsen others. However, weathering effects were also found to be very complex and dependent on multiple factors and generalizations were therefore not recommended. When examining the quantitative geochemistry of a rock type, analyzing weathered, or in other ways poor quality, surface should be avoided at least for the fact that XRF spectrometer excited fluorescence has been detected to originate mostly from depths of 0.01–5 mm (Potts et al. 1997a).

The problem with outcrop surface roughness and curviness of the drill core, both leaving a layer of air between the device and sample was also noticed to be part of the problem of low sum values in P-XRF analyses. Potts et al. (1997b) noticed that an air layer as thin as 1–2 mm is enough to cause major errors in the results, but with the help of scatter peak normalization a correction function for neutralizing surface roughness effects could be derived at least for elements with a higher atomic number. With further XRF outcrop studies and detailed descriptions of the coverings, it would be interesting to try and improve the corrections with Kumpula campus area outcrop and drill core materials.

On the base of this work, future studies regarding the improvement of P-XRF device should include problem solving of user effects by developing a portable light weight stand of some kind. Working in field would also benefit of a method for easily erasing weathered and contaminated surface layer thus also improving the surface smoothness. It would also be important to improve the detection limits and ability of detecting light elements, so that quantitative P-XRF analysis would become more accurate.

7.4 Drill core geochemistry: Omnian scans and P-XRF analyses

Taking the formerly mentioned weaknesses of P-XRF device into account, the decision of analyzing on average only one spot of each rock type unit in the drill core with P-XRF did not give reliable enough information about the geochemistry of the rock types. It would have been reasonable, but more time-consuming, to take multiple analyses of each unit and calculate average values.

Multiple P-XRF analyses from amphibolite sample A1 revealed the small-scale heterogeneity of the amphibolite. The P-XRF–WD-XRF quantitative application comparison suggests that SiO_2 , CaO , P_2O_5 and MnO concentrations of the drill core obtained with P-XRF can be examined quite confidently on average, although major element oxide sums are only 84.63 wt.% on average in ten amphibolite curved surface analyses.

In future studies, it would be interesting to include multiple P-XRF analyses and accurate WD-XRF quantitative analyses of the other rock types present in the drill core as well. This would bring more information and test the interpretations drawn so far based only on amphibolite about the accuracy of P-XRF.

Twelve sawed pieces of the amphibolite were supposed to give an idea of the possible change in geochemistry of amphibolite in relation to depth (Fig. 16). Study was conducted with WD-XRF Omnian scans and P-XRF, so that comparison between the methods could also be done, and double results were considered to provide more reliable information. The results did give a fairly wide geochemical range for the amphibolite, but correlation in relation to depth was not observed in this scale. On the other hand, the uncertainties of the analysis methods were in such a big role that

possible change in geochemistry in relation to depth might not even get detected this way.

WD-XRF Omnian scans from rock surfaces did not prove to be more accurate than P-XRF on average, but the major advantage of the method is the ability to detect light elements (Na, Al and Mg) better (Fig. 11). The relatively high correlation in CaO and K₂O analyses according to the method comparison based on 12 samples (Fig. 13) does not mean that the results are accurate, however. In case of K₂O, both methods give too low results when compared to WD-XRF quantitative application. It is also clear that P-XRF gives lower values for Al₂O₃ and MgO when compared to either Omnian scans or quantitative application. Al₂O₃ result obtained with Omnian scans from rock surface is quite accurate, but MgO is too low. Harker diagrams of the P-XRF results (Fig. 14) reveal the shortcomings of the initial rock type classification. Rock type identification of some analysis points would require revising.

Although the P-XRF results cannot be considered quantitative in general, relative abundances of the major element oxides (e.g. SiO₂, FeO_t, MgO) give adequate hints of the lithological changes in the core and a broad felsic-mafic discrimination could be made even without any visual logging data.

7.5 Considerations of petrology and a comparison to local geology

The rocks of Helsinki area show very little original or pre-orogeny features or textures (Laitala 1991, Kähkönen 1998). Only some sparse striping suggests a layered, probably a tuffaceous rock for the protolith, and Laitala (1991) thus assumes that areas amphibolites and hornblende gneisses were originally tuffaceous sediments, alkaline volcanic rocks and in some areas possibly alkaline plutonic rocks. During the collision of island arc and old Archean bedrock, low pressure greenschist/amphibolite facies metamorphism took place and shaped most of the rock types visible in Kumpula campus drill core today. Metamorphosis is thought to have happened in 15–20 km depth, at 500–700 °C (Laitala 1991, Kähkönen 1998).

The obtained geochemical and petrographic data was successfully connected to former presentation of the Helsinki and southern Finland geology by, e.g., Laitala (1991) and

Korsman and Koistinen (1998). However, the accurate petrology of the amphibolite is based on only one quantitative WD-XRF analysis and one thin section. More reliable interpretation would require multiple analyses and more quantitative trace element studies. Other three rock types presented are described only by their petrographical features and single Omnia scans results and thus have even more uncertain petrogenesis. More profound thin section works with samples from the whole length of the drill core would bring wider knowledge about the mineral compositions and heterogeneities of the described rock types. Future studies will bring more information and test the conclusions drawn below.

7.5.1 Amphibolite

Calc-alkaline magmas, that produce rock types typical of mature arcs, have high silica (see Equation [1]) and alkali contents (Best 2003). This kind of magma development was favored when Archean crust and an active island arc system collided and related continental growth was increasingly thickening the crust (Korsman and Koistinen 1998, Best 2003). Mg number (see Equation [2]), suggests the magma not to be primary.

Increasing temperature and the presence of fluids during the metamorphism changed the texture of the amphibolite to more granoblastic. Ca-Al-silicates, albite and aluminous chlorite together probably formed hornblende and more Ca-rich plagioclase (Best 2003).

TAS diagram (Fig. 9) and Zr/Ti–Nb/Y diagram (Fig. 10.A) give different results for the protolith of the amphibolite, which underlines the importance of considering the alkali mobilization when studying the petrogenesis of metamorphic rocks. It would be interesting to see more precise plotting of the amphibolite in the Zr/Ti – Nb/Y diagram with better trace element results obtained e.g. with inductively coupled mass spectrometry (ICP-MS).

Comparing to whole rock analyses of nearest temporally related amphibolite units (Fig. 10, Fig. 16, Table 7), SiO₂ wt.% seems to be higher in quantitative WD-XRF analysis of the sample A1 in this work (57.41 wt.%) than in the other amphibolite units on average (48.67 wt.%). Sample A1 values for Al₂O₃ (15.37 wt.%), Na₂O (3.93 wt.%) and K₂O

(1.65 wt.%) are also higher than average values of the nearest units (14.83 wt%, 3.11 wt.% and 0.86 wt.% respectively). The rest of the major element oxide values are lower. This indicates the amphibolite sample A1 chosen for this work to be more felsic than the selected samples of GTK. Utilizing the ICP-MS results of the same analysis points (Appendix VII) and plotting the results in Zr/Ti–Nb/Y diagram (Fig. 10.A) set the values is basaltic, basaltic-andesite and alkali basalt areas. Sample number 6 from Sääksjärvi plots very close to sample A1. GTK samples are from quite a large area (Fig. 16), each being quite far from Kumpula campus drill hole.

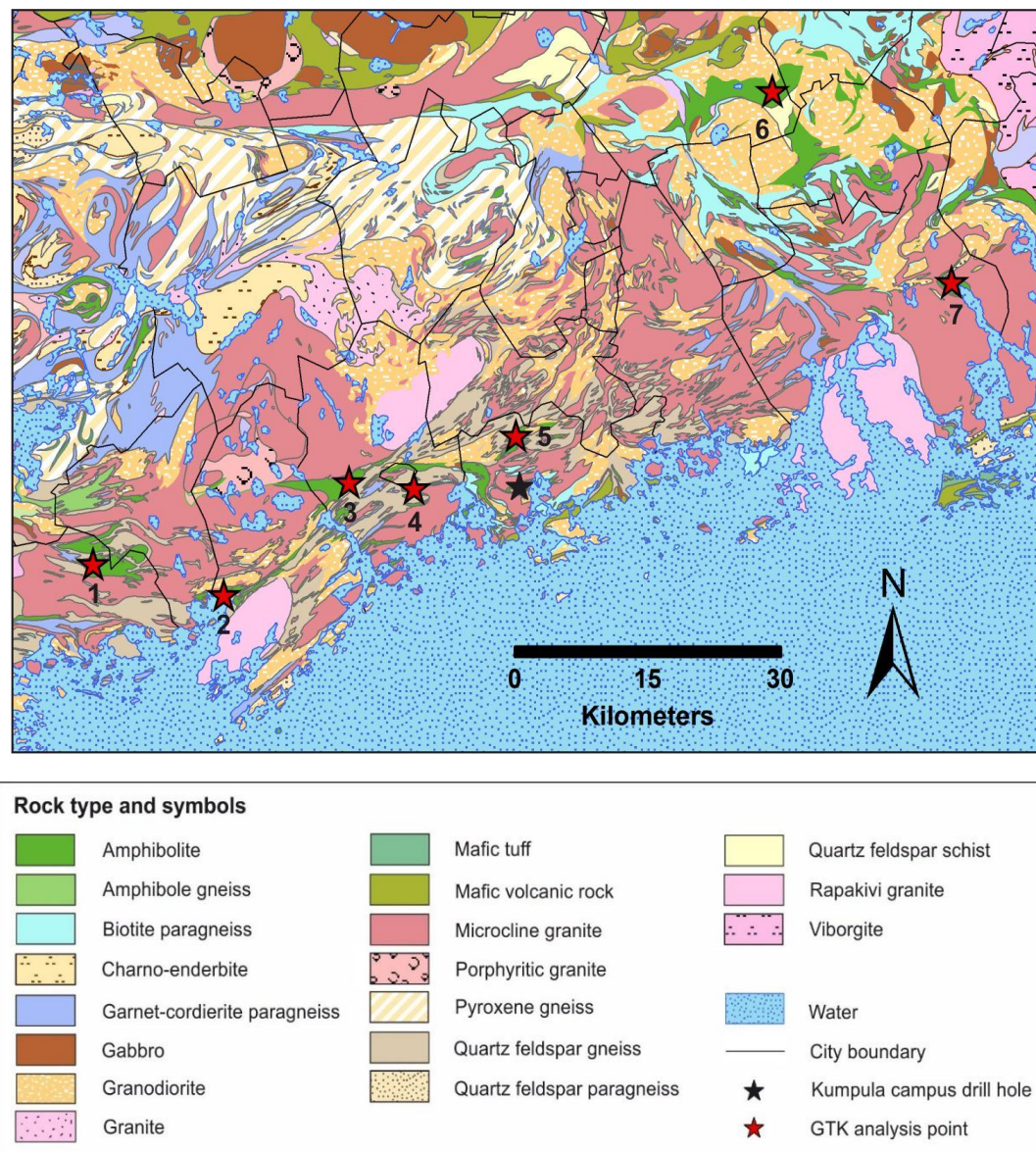


Figure 16. Locations of the seven closest analysis points of GTK The rock geochemical database of Finland from temporally related amphibolite units in relation to Kumpula campus drill hole. Bedrock map after GTK. Basemap of Finland and city boundaries © NLS.

Table 7. Whole-rock geochemistry of selected temporally related amphibolite units. Results are obtained with Phillips PW1480 WD-XRF with pressed powder pellets. Data from GTK rock geochemical database of Finland (Rasilainen et al. 2007).

Point ID	1	2	3	4	5	6	7	
Location	Inkoo	Kirkkonummi	Espoo	Espoo	Helsinki	Sääksjärvi	Porvoo	
Rock type	Amp.	Amp.	Amp.	Amp.	M.volc.	Amp.	M.volc.	avg.
SiO ₂ (wt.%)	45.40	47.10	53.00	50.70	51.40	50.10	43.00	48.67
TiO ₂	2.70	0.64	0.62	2.38	0.96	1.77	2.44	1.64
Al ₂ O ₃	12.10	15.60	16.70	13.80	16.70	15.90	13.00	14.83
FeOt	15.93	7.77	7.76	13.32	9.90	8.73	11.25	10.66
MnO	0.26	0.16	0.16	0.24	0.19	0.15	0.17	0.19
MgO	5.24	8.57	4.36	3.41	3.96	4.24	5.53	5.04
CaO	8.22	11.60	8.09	7.16	6.62	7.69	11.40	8.68
Na ₂ O	2.19	1.74	2.75	3.06	4.77	3.63	3.62	3.11
K ₂ O	1.07	0.28	0.68	0.83	0.72	1.62	0.85	0.86
P ₂ O ₅	0.12	0.03	0.10	0.24	0.20	0.93	0.30	0.27
Sum	93.23	93.48	94.21	95.13	95.42	94.76	91.55	93.97
Ba (ppm)	163	61.8	213	179	392	596	459	
Cl	741	141	261	483	80.1	505	146	
S	220	737	114	591	78	2270	1500	
Cr	<19	491	47.1	27	24	27	96.1	
Cu	30.1	72	17	33.9	<17	129	188	
Ga	22	19	23.2	23.7	29	29.8	31.4	
Nb	<7	<7	<7	7.6	<7	22.5	45.9	
Ni	<14	103	<14	15	<14	38.4	122	
Pb	16	<14	22	23	27	16	15	
Rb	66.1	14.6	15.3	20.7	33.1	141	29	
Sr	121	153	272	149	224	1200	323	
V	974	185	184	459	209	221	395	
Y	30.6	9.1	16	46.7	17.4	20.3	21.3	
Zn	175	77	92.3	135	131	141	121	
Zr	84.8	21	70.5	194	115	186	195	

Mo excluded (all values <LOD)

Amp.= amphibolite

M.volc.= mafic volcanite

7.5.2 Other rock types

Diopside-actinolite skarn indicates low temperature metamorphic conditions with active metasomatism. Laitala (1991) states that metasomatism between the impure limestones, gneissic layers and gneissic surrounding rocks of the area formed skarn. Diopside has partly altered to actinolite, plagioclase has albitized and released Ca and Al that served as building material for epidote and zoisite. Free Ca together with Ti-oxides probably formed sphenes (Best 2003).

Low-temperature metamorphic conditions formed also actinolite rocks with high MgO content. All the clinopyroxenes altered to actinolite and some chlorite (Best 2003). The grain size is smaller than that of amphibolites and mineral grains are subhedral or anhedral. Granite has probably formed later during the orogeny and intruded the

metamorphic rocks following their structural control (Laitala 1991, Korsman and Koistinen 1998).

8. CONCLUSIONS

Amphibolite, granite, actinolite rock and diopside-actinolite skarn among with migmatite and gneiss are found in Kumpula campus bedrock. Variation in rock types is wider than bedrock map suggests but all can be connected to former geological interpretations of the Helsinki area. The amphibolite of Kumpula seems more felsic than nearest temporally related amphibolite units. To specify the petrogenesis of amphibolite and other described rock types, would it require more extensive thin section and trace element studies.

WD-XRF Omnian scans and quantitative application suggest almost similar results for fused bead of amphibolite sample A1. Changing the sample type to solid rock surface of sample A1 introduces heterogeneity related problems to the quantitative determination of Omnian scans. Omnian scans and P-XRF analyses of twelve sawed pieces of the amphibolite from different depths of the drill core suggest quite wide compositional range for the amphibolite. The cause is probably a combination of amphibolite heterogeneity and methodology caused variation. Correlation along depth cannot be observed. Omnian scans and P-XRF results seem to correlate best with CaO and K₂O. MgO and Al₂O₃ values are always lower with P-XRF.

Analyzing the drill core surface with P-XRF was found to be useful, fast and easy method for detecting broad geochemical changes although major element oxide sum is only 84.00 wt.% on average. Comparing ten P-XRF analyses of sample A1 to WD-XRF quantitative application analysis of fused bead revealed that P-XRF SiO₂ wt.% value is quite accurate on average. Other relatively accurate P-XRF results on average are for CaO and MnO. On the other hand, MgO, K₂O and Al₂O₃ are poorly detected with P-XRF device.

Outcrop studies conclude that the quality of the analysis surface has a major impact on the success of P-XRF analyses. Considerable factors are smoothness, grain size,

weathering, pollution, alteration and organisms such as lichen and moss. Major oxide sum values of outcrop studies are very low, yet enhanced concentrations of Cl, P and S are detected especially on poor quality surfaces. The reasons for enhancements would require further research.

Comparing to other introduced methods, utilizing P-XRF requires much more attention from the user during the analyses. However, WD-XRF quantitative method, WD-XRF Omnia scans and P-XRF were all proven to be useful methods in different contexts. Selection depends on the study and the need for further analyses should be evaluated in each case.

8. ACKNOWLEDGEMENTS

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9. REFERENCES

- Best, M.G. 2003. *Igneous and Metamorphic petrology*. 2nd edition. Blackwell Science Ltd, Malden, 729 p.
- Ewart, A. 1982. The mineralogy and petrology of Tertiary-Recent orogenic volcanic rocks with special reference to the andesitic-basaltic compositional range. In: Thorpe, R.S. (Eds.), *Andesites: Orogenic Andesites and Related Rocks*.
- Geological survey of Finland, 2017. Bedrock map of Finland scale-free, version 2.1.
- Hatakka, T., Nuottimäki, K., Sarala, P., Taivalkoski, A. and Tarvainen, T. 2016. Kenttä-XRF-analysaattorin soveltuvuus geokemiallisiin taustapitoisuustutkimuksiin. Geological survey of Finland, Espoo, archive report 97/2015, 115 p.
- Heikkilä, P. 2015. Mineralogy laboratory manual. Department of Geosciences and Geography, University of Helsinki, 18 p.
- Irvine, T.N. and Baragar, W.R.A. 1971. A Guide to the Chemical Classification of the Common Volcanic Rocks. *Canadian Journal of Earth Sciences*, 8, 523–548.
- Kivinen, A. (GRM-Services Oy) 2016. Kampusreikä: Geofysikaaliset reikämittaukset, work report, 13 p.
- Korsman, K. and Koistinen, T. Suomen kallioperän yleispiirteet. 1998. In Lehtinen, M., Nurmi, P. and Rämö, T. (Eds.). *Suomen kallioperä: 3000 vuosimiljoonaa*. The Geological Society of Finland, Helsinki, 93–104.
- Kramar, U. 1997. Advances in energy-dispersive X-ray fluorescence. *Journal of Geochemical Exploration* 58, 73–80.
- Kretz, R. 1983. Symbols for rock-forming minerals. *American Mineralogist* 68, 277–279.
- Kukkonen, I.T., Koivisto, E. and Whipp, D. 2016. Helsinki University Kumpula campus drillhole project. In: Kukkonen et al. (Eds.), *Lithosphere 2016 – Ninth Symposium on the Structure, Composition and Evolution of the Lithosphere in Finland*. Programme and Extended Abstracts, Espoo, Finland, November 9–11, 2016. Institute of Seismology, University of Helsinki, Report S-65, 166 p.
- Kuno, H. 1986. Differentiation of basalt magmas. In: Hess, H.H and Poldervaart, A. (Eds.) *Basalts: The Poldervaart treatise on rocks of basaltic composition*, 2, Interscience, New York, 623–688.
- Kähkönen, Y. Svekofenniset liuskealueet. 1998. In: Lehtinen, M., Nurmi, P. and Rämö, T. (Eds.). *Suomen kallioperä: 3000 vuosimiljoonaa*. The Geological Society of Finland, Helsinki, 199–227.
- Laitala, M. 1991. Pre-Quaternary rocks of the Helsinki map-sheet area. Explanation to the maps of pre-quaternary rocks. Geological survey of Finland. Sheet 2034.
- Le Bas, M.J., Le Maitre, R.W., Streckeisen, A. and Zanettin, B. 1986. A Chemical Classification of Volcanic Rocks Based on the Total Alkali-Silica Diagram. *Journal of Petrology* 27, part 3, 745–750.
- Liritzis, I. and Zacharias, N. 2011. Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations. In: Shackley, M.S. (Eds.). *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, 109–142.
- Marguí, E., Grieken, R. van, 2013. *X-Ray Fluorescence Spectrometry and Related Techniques: An Introduction*. Momentum Press, New York, 142 p.
- Marguí, E., Hidalgo, M., Queralt, I., Meel, K. van and Fontàs, C. 2012. Analytical capabilities of laboratory, benchtop and handheld X-ray fluorescence systems for detection of metals in aqueous samples pre-concentrated with solid-phase extraction disks. *Spectrochimica Acta Part B* 67, 17–23.
- Markey, A.M., Clark, C.S., Succop, P.A. and Roda, S. 2008. Determination of the Feasibility of Using a Portable X-Ray Fluorescence (XRF) Analyzer in the Field for Measurement of Lead Content of Sieved Soil. *Journal of Environmental Health* 70, 24–29.
- National Land Survey of Finland. 2016. General map of Finland, 1: 1 000 000.
- National Land Survey of Finland. 2016. Basemap of Helsinki, sheet L4133L.

- Nironen, M., Proterotsooiset orogeeniset syväkivet. In: Martti Lehtinen, Pekka Nurmi and Tapani Rämö (Eds.) 1998. Suomen kallioperä: 3000 vuosimiljoonaa. The Geological society of Finland, Helsinki 375 p.
- Norrish, K. and Chappell, B.W. 1967. X-ray Fluorescence Spectroscopy. In: Zussman, J. (Eds.) Physical methods in determinative mineralogy. Academic Press, London, 161–214.
- Norrish, K. and Hutton, J.T. 1968. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochimica et Cosmochimica Acta*, 33, 431–453.
- Pajunen, M., Airo, M.-L., Elminen, T., Mänttari, I., Niemelä, R., Vaarma, M., Wasenius, P. and Wennerström, M. 2008. Tectonic evolution of the Svecofennian crust in southern Finland. In: Pajunen, M. (Eds.). Tectonic evolution of the Svecofennian crust in southern Finland – a basis for characterizing bedrock technical properties. Geological Survey of Finland, Special Paper 47, 15–160.
- PANalytical. 2018. Omnian method. Page visited 5.4.2018. <http://www.panalytical.com/Xray-fluorescence-software/Omnian.htm>
- Parsons, C., Grabulosa, E.M., Pili, E., Floor, G.H., Roman-Ross, G. and Charlet, L. 2013. Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: Considerations for sample preparation and measurement conditions. *Journal of Hazardous Materials* 262, 1213–1222.
- Pearce, J.A. 1996. A User's guide to Basalt Discrimination Diagrams. In: Wyman, D.A. (Eds.) Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulphide Exploration. Geological Association of Canada, Short Course Notes 12, 79–113.
- Penttilä, K., Kukkonen, I., Heinonen, J.S., Räisänen, M. and Valtonen, R. 2016. Logging and lithology of the Kumpula Campus drill hole. Poster presentation in: Lithosphere 2016 – Ninth Symposium on the Structure, Composition and Evolution of the Lithosphere in Finland. Espoo, Finland, November 9–11.
- Potts, P. J., Williams-Thorpe, O. and Webb, P.C. 1997a. The Bulk Analysis of Silicate Rocks by Portable X-Ray Fluorescence: Effect of Sample Mineralogy in Relation to the Size of the Excited Volume. *Geostandard Newsletter*, 21, 29–41.
- Potts, P. J., Webb, P. C. and Williams-Thorpe, O. 1997b. Investigation of a Correction Procedure for Surface Irregularity Effects Based on Scatter Peak Intensities in the Field Analysis of Geological and Archaeological Rock Samples by Portable X-ray Fluorescence Spectrometry. *Journal of Analytical Atomic Spectrometry*, 12, 769–776.
- Potts, P.J. and Webb, P.C. 1992. X-ray fluorescence spectrometry. *Journal of Geochemical Exploration* 44, 251–296.
- Potts, P.J., Bernardini, F., Jones, M.C., Williams-Thorpe, O. and Webb, P.C. 2006. Effects of weathering on *in situ* portable X-ray fluorescence analyses of geological outcrops: dolerite and rhyolite outcrops from the Preseli Mountains, South Wales. *X-Ray Spectrometry* 35, 8–18.
- Rasilainen, K., Lahtinen, R. and Bornhorst, T.J. 2007. The Rock Geochemical Database of Finland. Geological survey of Finland. Report of Investigation 164.
- Rowe, H., Hughes, N. and Robinson, K. 2012. The quantification and application of handheld energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and geochemistry. *Chemical Geology* 324–325, 122–131.
- Sarala, P., Taivalkoski, A. and Valkama, J. 2014. Kannettavan XRF-analysaattorin käyttö moreenigeokemiallisessa tutkimuksessa. Geological survey of Finland, Rovaniemi, archive report 120/2014, 22 p.
- Shrivastava, P., O'Connell, S. and Whitley, A. 2005. Handheld X-Ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment. Proceedings of the 2005 IEEE International Symposium on Electronics and the Environment, New Orleans, LA, USA, May 16–19, 2005, 157–162.
- Winchester, J.A. and Floyd, P.A. 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chemical Geology*, 20, 325–343.

- Worley, C.G., Wiltshire, S.S., Miller, T.C., Havrilla, G.J and Majidi, V. 2006. Detection of visible and latent fingerprints by micro-X-ray fluorescence. *Advances in X-ray Analysis*, 49, 363–368.
- Young, K.E., Evans, C.A., Hodges, K.V., Bleacher, J.E. and Graff, T.G. 2016. A review of the handheld X-ray fluorescence spectrometer as a tool for field geologic investigations on Earth and in planetary surface exploration. *Applied Geochemistry* 72, 77–87.

APPENDIX I: Sawed surface P-XRF data of the amphibolite sample A1

ID	1	2	3	4	5	6	7	8	9	10
SiO ₂ (wt.%)	59.98	59.91	59.67	56.80	57.48	56.52	54.73	58.32	57.37	58.62
TiO ₂	0.77	0.79	0.77	0.82	0.95	0.76	0.76	0.70	0.82	0.87
Al ₂ O ₃	12.12	11.81	11.40	10.14	10.76	11.13	9.69	11.33	10.41	10.47
FeO _t	5.15	5.56	5.35	6.84	6.55	5.70	6.28	6.42	6.87	7.21
MnO	0.09	0.09	0.08	0.14	0.11	0.10	0.13	0.13	0.14	0.15
MgO	0.99	1.83	1.46	1.81	1.84	1.52	1.53	1.33	2.25	2.52
CaO	5.91	6.18	5.82	6.63	5.86	6.21	6.37	6.99	6.54	6.68
K ₂ O	1.19	1.26	1.30	1.15	1.54	1.22	1.01	0.97	1.13	1.17
P ₂ O ₅	0.20	0.16	0.18	0.12	0.22	0.22	0.12	0.17	0.20	0.19
Sum	86.41	87.61	86.03	84.44	85.32	83.37	80.61	86.37	85.72	87.86
Ba (ppm)	510	540	530	530	490	500	520	520	530	560
Cl	n.d.	230	180	n.d.	80	480	n.d.	150	70	270
S	n.d.	400	150	270	230	n.d.	150	180	170	220
Cr	200	240	210	260	250	210	210	200	260	320
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	60
Rb	20	20	20	20	30	20	20	20	20	20
Sn	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40
Sr	250	240	260	220	230	240	220	240	210	200
V	200	200	200	260	270	250	230	280	250	250
Zn	30	40	30	40	40	30	40	30	40	50
Zr	150	30	40	50	50	30	80	140	60	40

Excluded elements (all values <LOD): Cu,Nb,Co,As,Se,Mo,Pd,Ag,Cd,Sb,W,Au,Pb,Bi

APPENDIX II: Curved surface P-XRF data of the amphibolite sample A1

ID	1	2	3	4	5	6	7	8	9	10
SiO ₂ (wt.%)	56.14	58.09	58.37	57.58	59.08	54.93	53.38	54.25	58.74	60.81
TiO ₂	0.83	0.87	0.69	0.87	0.56	1.04	0.99	1.12	1.15	0.86
Al ₂ O ₃	11.66	10.63	11.95	10.36	11.41	9.81	10.37	11.04	11.79	12.30
FeO _t	6.76	6.06	4.70	5.67	4.84	7.87	6.42	6.27	6.75	5.80
MnO	0.13	0.10	0.06	0.10	0.09	0.15	0.10	0.11	0.11	0.10
MgO	2.35	1.39	1.43	1.71	1.71	1.74	1.47	2.08	2.37	1.86
CaO	6.63	5.62	5.69	5.26	6.27	6.25	5.36	5.68	5.21	5.83
K ₂ O	1.23	1.40	1.24	1.52	0.92	1.46	1.73	1.61	1.85	1.52
P ₂ O ₅	0.18	0.20	0.17	0.10	0.23	0.24	0.25	0.30	0.22	0.19
Sum	85.91	84.36	84.30	83.17	85.11	83.48	80.08	82.47	88.17	89.26
Ba (ppm)	580	520	440	560	470	570	550	580	630	510
Cl	250	330	210	1020	490	350	290	460	380	100
S	370	240	390	300	370	290	230	330	380	240
Cr	260	250	210	230	170	340	220	240	290	220
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	60	n.d.	n.d.	n.d.	n.d.
Rb	20	30	20	20	20	30	30	20	30	20
Sn	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	30
Sr	250	230	270	230	270	200	210	220	230	240
V	230	280	180	240	170	310	240	280	250	210
Zn	40	50	30	40	30	50	40	40	40	30
Zr	20	50	70	60	40	30	50	70	40	70

Excluded elements (all values <LOD): Cu,Nb,Co,As,Se,Mo,Pd,Ag,Cd,Sb,W,Au,Pb,Bi

APPENDIX III: WD-XRF Omnian scans data of the drill core samples

ID	t1s1	t1s2	t1s3	t1s4	t1s5	t1s6	t1s7	t1s8	t1s9	t1s10	t1s11	t1s12	t2	t3	t4
Depth (m)	3.90	36.00	63.35	88.95	105.35	128.30	156.00	203.00	241.55	323.20	336.70	361.60	351.50	35.00	145.70
SiO ₂ (wt.%)	50.58	50.48	51.23	53.95	55.62	48.22	49.32	56.56	56.77	50.75	51.96	59.32	72.04	43.19	51.91
TiO ₂	0.86	1.00	0.78	0.90	0.83	0.88	0.86	0.78	0.72	0.97	0.88	0.75	0.08	0.58	0.68
Al ₂ O ₃	16.34	15.80	18.07	14.89	15.33	15.76	16.85	16.48	16.16	15.71	17.36	16.55	13.75	8.20	18.15
FeOt	5.82	6.93	4.46	5.43	5.53	7.46	4.71	5.57	4.33	6.53	6.61	3.50	0.72	8.87	1.35
MnO	0.11	0.11	0.07	0.11	0.10	0.16	0.11	0.09	0.06	0.09	0.13	0.10	0.02	0.17	0.04
MgO	4.09	5.40	3.63	5.15	3.98	7.45	4.90	4.80	5.65	5.39	4.09	3.36	0.35	17.73	5.33
CaO	7.03	6.18	7.29	5.93	5.62	3.78	6.27	3.39	2.22	8.09	5.56	2.69	1.20	7.30	10.59
Na ₂ O	3.92	3.91	4.94	3.88	3.81	3.36	4.55	4.27	4.43	4.54	4.64	5.13	4.08	0.30	4.30
K ₂ O	0.93	1.96	0.55	1.51	1.52	3.90	1.53	2.30	3.75	0.68	1.76	2.75	4.23	3.81	0.92
P ₂ O ₅	0.25	0.25	0.25	0.22	0.21	0.18	0.19	0.18	0.19	0.27	0.20	0.22	0.05	0.17	0.26
Sum	89.93	92.02	91.27	91.96	92.55	91.15	89.29	94.40	94.28	93.02	93.19	94.37	96.53	90.30	93.52
Cl (ppm)	110	150	180	140	110	180	100	160	120	150	170	570	190	140	80
F	0	1220	0	0	0	1890	1500	0	2130	1600	1590	1400	0	1390	0
S	140	80	40	90	70	80	30	40	40	850	240	70	60	60	50
Ba	230	400	170	210	360	370	150	430	260	90	210	130	360	140	200
Co	0	0	60	0	0	0	0	0	0	0	0	0	0	70	0
Cr	180	240	180	290	140	170	180	140	190	270	190	180	0	2530	170
Cu	20	0	30	30	30	30	30	20	20	70	50	20	20	30	30
Ga	30	20	30	20	20	20	20	20	20	20	30	20	20	20	20
Nb	10	10	10	10	10	10	10	10	10	10	10	10	0	0	10
Ni	50	80	40	80	60	60	70	60	70	60	50	40	40	880	60
Pb	20	0	20	20	0	30	30	30	20	0	20	0	40	0	0
Rb	30	90	0	50	50	180	110	70	230	10	120	240	180	270	40
Sr	420	610	450	240	320	210	270	220	120	350	280	140	80	10	320
V	200	220	200	200	160	190	190	150	140	260	180	140	0	150	180
Y	0	0	20	0	0	0	0	0	0	0	0	0	0	0	0
Zn	60	40	40	40	40	130	60	50	100	50	70	100	10	100	30
Zr	120	160	140	70	120	90	100	80	100	110	120	80	70	50	90

Sample IDs: t1s1–t1s12= amphibolite, t2= granite, t3= actinolite rock, t4= diopside-actinolite skarn

APPENDIX IV: P-XRF data of the drill core samples

ID	t1s1	t1s2	t1s3	t1s4	t1s5	t1s6	t1s7	t1s8	t1s9	t1s10	t1s11	t1s12	t2	t3	t4
Depth (m)	3.90	36.00	63.35	88.95	105.35	128.30	156.00	203.00	241.55	323.20	336.70	361.60	351.50	35.00	145.70
SiO ₂ (wt.%)	64.22	55.60	54.13	57.59	64.51	59.40	55.00	63.15	60.75	55.95	57.11	63.73	77.67	47.38	57.43
TiO ₂	0.43	0.96	0.77	0.91	0.57	0.92	0.82	0.85	0.73	1.07	0.82	0.98	0.10	0.52	0.80
Al ₂ O ₃	13.42	13.01	12.84	11.04	11.38	12.47	14.01	12.54	12.70	12.89	12.98	12.00	9.64	5.92	13.31
FeOt	3.64	6.67	5.61	6.40	5.01	6.15	5.01	5.25	4.70	7.55	6.43	5.21	1.17	8.55	1.54
MnO	0.06	0.11	0.08	0.15	0.09	0.10	0.11	0.06	0.07	0.11	0.13	0.15	0.00	0.17	0.04
MgO	0.53	2.60	1.87	2.55	1.77	2.35	2.07	1.84	2.61	2.36	1.98	2.44	0.45	8.83	2.47
CaO	7.43	7.05	8.38	6.42	6.38	3.55	7.12	3.40	2.47	9.32	5.91	2.61	1.09	8.25	11.76
K ₂ O	0.50	1.38	0.45	1.47	0.83	2.79	1.37	2.11	3.18	0.58	1.33	2.91	3.32	2.97	0.82
P ₂ O ₅	0.13	0.22	0.24	0.16	0.18	0.13	0.17	0.23	0.16	0.27	0.17	0.23	0.19	0.11	0.35
Sum	90.35	87.60	84.37	86.68	90.72	87.87	85.68	89.43	87.37	90.11	86.87	90.26	93.64	82.71	88.51
Ba (ppm)	370	580	340	440	410	510	390	580	440	260	260	300	500	310	400
Cl	170	0	0	90	0	0	0	0	0	0	0	0	0	210	0
S	200	0	110	90	150	0	0	0	0	3820	200	0	0	90	100
Ag	100	120	90	110	100	90	110	80	90	110	90	90	70	110	90
Bi	0	0	0	0	0	0	10	0	0	10	0	0	10	0	0
Cr	170	320	300	370	210	270	290	270	260	420	280	270	40	2300	300
Cu	0	0	0	0	0	0	0	0	0	60	0	0	0	0	0
Nb	10	10	10	10	10	10	10	10	10	10	10	10	10	0	10
Ni	0	0	0	0	0	0	50	0	0	60	0	0	0	790	0
Pb	10	10	10	10	10	10	10	10	30	10	10	10	30	0	10
Pd	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10
Rb	0	30	0	20	10	70	50	30	110	10	40	150	90	100	30
Sn	20	0	20	0	0	0	40	0	30	0	0	0	20	30	0
Sr	350	460	310	160	230	160	200	160	90	250	220	90	60	10	220
V	140	310	300	280	220	220	230	200	280	300	280	260	0	290	220
W	0	0	60	0	0	0	0	60	0	0	0	0	0	0	0
Zn	10	30	20	40	30	80	60	30	90	40	40	120	20	90	20
Zr	70	100	90	10	70	30	70	30	50	80	50	20	60	40	180

Excluded elements (all values <LOD): As, Au, Cd, Co, Mo, Sb, Se

Sample IDs: t1s1–t1s12= amphibolite, t2= granite, t3= actinolite rock, t4= diopside-actinolite skarn

APPENDIX V: P-XRF data of the whole drill core analyses

ID	k1	k2	k3	k4	k5	k6	k7	k8	k9	k10	k11	k12	k13	k14	k15
Rock type	Amp	Grt	Diop	Amp	Amp	Grt	Act	Grt	Act	Amp	Grt	Amp	Grt	Grt	Grt
Depth (m)	2.00	10.00	16.47	20.00	22.00	29.00	31.00	34.00	35.00	36.00	43.00	46.00	49.00	52.00	54.30
SiO ₂ (wt.%)	49.71	68.95	56.27	50.78	55.87	68.04	44.99	66.68	44.99	52.59	71.66	51.21	69.36	60.71	73.04
TiO ₂	0.96	0.13	0.65	0.66	0.44	0.03	0.64	0.01	0.51	0.91	0.26	1.17	0.09	0.66	0.10
Al ₂ O ₃	9.89	7.37	13.33	10.58	9.81	9.03	8.67	9.76	5.13	12.05	8.75	10.92	7.97	12.65	7.67
FeOt	7.91	1.39	1.22	4.56	3.67	0.25	11.24	0.15	8.45	7.24	1.37	7.94	1.05	5.68	0.75
MnO	0.12	0.00	0.03	0.11	0.15	0.00	0.24	0.00	0.15	0.11	0.00	0.17	0.00	0.10	0.00
MgO	2.16	0.00	1.24	2.26	4.12	0.49	5.49	0.00	7.11	2.07	0.00	2.50	0.00	1.84	0.00
CaO	7.32	1.06	10.05	8.41	10.98	2.29	12.07	1.47	8.25	6.78	2.63	9.10	0.24	7.22	2.05
K ₂ O	1.06	3.49	1.03	0.50	0.30	0.68	0.79	1.13	2.99	1.49	0.92	0.79	3.42	0.76	0.60
P ₂ O ₅	0.19	0.00	0.10	0.12	0.00	0.08	0.00	0.38	0.00	0.23	0.11	0.25	0.00	0.14	0.08
Sum	79.31	82.40	83.90	77.98	85.34	80.89	84.14	79.57	77.58	83.47	85.71	84.04	82.12	89.75	84.28
Ba (ppm)	550	740	290	270	350	200	230	290	330	640	510	450	710	430	130
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	140	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	990	220	210	130	130	320	980	320	n.d.	270	130	130	n.d.	170	100
Bi	n.d.	20	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.
Cr	370	60	170	330	370	n.d.	1120	120	1600	330	70	460	60	280	80
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	230	n.d.	700	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	40	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	n.d.	20
Rb	20	60	n.d.	n.d.	n.d.	n.d.	n.d.	20	110	30	20	n.d.	60	n.d.	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	270	90	330	250	130	90	70	140	n.d.	430	160	240	60	290	80
V	290	n.d.	120	230	280	n.d.	420	50	230	280	50	380	40	240	60
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	50	20	20	40	40	n.d.	80	n.d.	80	40	n.d.	50	n.d.	40	20
Zr	140	80	80	80	40	20	30	n.d.	30	50	110	30	70	60	50

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k15.5	k16	k17	k18	k19	k20	k21	k22	k23	k24	k25	k26	k27	k28	k29
Rock type	Act	Amp	Act	Grt	Act	Mgm	Grt	Mgm	Grt	Diop	Grt	Amp	Grt	Amp	Amp
Depth (m)	59.00	61.00	64.40	66.00	68.00	70.40	76.05	78.25	81.00	82.00	83.00	84.00	85.30	88.50	94.60
SiO ₂ wt. %	46.21	53.96	46.68	66.92	50.24	53.86	68.12	54.93	74.71	54.74	67.93	59.02	73.82	55.91	54.28
TiO ₂	0.97	0.60	0.43	0.32	0.34	0.75	0.09	0.65	0.09	0.87	0.05	0.45	0.01	0.82	0.66
Al ₂ O ₃	13.50	13.24	6.58	10.51	9.30	11.52	10.16	11.78	7.76	11.64	7.58	10.75	8.24	11.68	11.56
FeOt	10.29	4.17	9.77	1.80	8.39	3.93	0.56	2.22	0.94	1.33	0.34	1.79	0.19	5.85	4.65
MnO	0.19	0.05	0.22	0.00	0.23	0.08	0.00	0.06	0.00	0.05	0.00	0.08	0.00	0.13	0.09
MgO	3.88	1.58	5.50	0.85	4.91	2.24	0.60	2.17	0.44	1.73	0.00	1.32	0.39	1.93	2.22
CaO	10.15	8.29	10.73	3.22	10.71	8.54	2.57	6.72	1.27	10.13	1.32	7.15	0.37	5.86	4.63
K ₂ O	1.26	0.51	0.95	1.04	0.59	0.63	0.71	1.08	2.31	0.43	2.86	0.52	3.50	1.40	1.64
P ₂ O ₅	0.09	0.16	0.00	0.13	0.11	0.22	0.00	0.18	0.15	0.27	0.00	0.16	0.00	0.23	0.22
Sum	86.55	82.55	80.86	84.78	84.82	81.77	82.80	79.79	87.68	81.19	80.08	81.25	86.53	83.80	79.96
Ba ppm	410	260	320	810	270	360	180	260	420	240	330	280	450	310	510
Cl	n.d.	n.d.	130	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	140	110	n.d.	n.d.	n.d.	n.d.	340	200	210	n.d.	n.d.	150	210	150	n.d.
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.
Cr	420	240	1350	70	1060	260	140	240	50	190	90	170	130	280	280
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	260	n.d.	200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	30	n.d.	30	n.d.	n.d.
Rb	20	n.d.	30	30	n.d.	n.d.	n.d.	30	40	n.d.	40	n.d.	50	20	60
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	170	360	60	270	150	250	140	270	60	210	60	140	60	190	120
V	480	290	350	50	300	230	n.d.	170	90	180	n.d.	170	n.d.	290	220
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	90	20	130	n.d.	140	20	n.d.	40	n.d.	20	n.d.	30	n.d.	50	40
Zr	20	70	n.d.	190	n.d.	70	40	80	20	120	n.d.	40	50	100	80

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k30	k31	k32	k34	k35	k36	k37	k38	k40	k42	k43	k44	k45	k46	k47
Rock type	Amp	Grt	Act	Amp	Mgm	Mgm	Mgm	Diop	Diop	Grt	Act	Grt	Grt	Amp	Amp
Depth (m)	95.10	98.00	99.45	105.27	106.10	109.70	111.60	113.40	118.00	124.40	125.40	125.65	127.00	127.40	130.10
SiO ₂ (wt.%)	50.85	69.29	56.14	58.41	61.38	67.63	56.10	55.95	57.05	59.58	49.81	61.76	62.79	62.01	52.47
TiO ₂	0.64	0.30	0.73	0.77	0.48	0.31	0.47	0.32	0.44	0.58	0.39	0.28	0.50	0.81	1.29
Al ₂ O ₃	11.28	10.04	12.19	11.62	11.48	11.12	11.82	11.69	12.01	12.67	7.80	13.91	11.44	10.77	10.65
FeOt	8.53	1.47	7.82	5.96	2.35	1.78	2.23	1.24	1.00	1.26	8.40	1.73	2.61	6.06	8.44
MnO	0.18	0.00	0.13	0.12	0.05	0.00	0.05	0.02	0.02	0.02	0.17	0.00	0.02	0.07	0.19
MgO	3.03	0.48	2.25	1.30	1.29	0.94	1.77	1.51	1.27	1.32	4.81	0.57	0.68	2.15	2.17
CaO	10.57	3.03	5.50	6.15	7.27	3.29	7.44	9.48	8.83	8.33	10.28	1.55	3.40	2.55	5.88
K ₂ O	0.55	0.97	1.00	1.35	0.50	1.17	0.56	0.43	0.52	0.48	0.62	4.35	1.42	3.07	2.10
P ₂ O ₅	0.14	0.68	0.22	0.21	0.18	0.16	0.15	0.11	0.16	0.00	0.19	0.15	0.19	0.08	0.18
Sum	85.77	86.28	85.98	85.89	84.97	86.40	80.60	80.74	81.30	84.26	82.47	84.30	83.06	87.57	83.38
Ba (ppm)	300	510	440	560	350	910	340	350	330	300	450	900	730	770	400
Cl	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	n.d.	160	770	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	250	n.d.	180	120	3200
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	320	90	270	180	170	70	200	110	150	130	770	120	130	270	400
Cu	n.d.	n.d.	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	120
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	250	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rb	n.d.	20	30	30	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	130	20	80	40
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	250	270	190	240	240	310	240	310	240	210	160	240	310	180	120
V	400	100	300	220	120	n.d.	180	120	140	90	270	60	60	260	360
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	70	20	80	40	20	20	30	n.d.	n.d.	n.d.	90	20	20	80	70
Zr	30	170	90	80	20	180	120	90	90	150	60	270	250	40	40

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k48	k49	k50	k51	k53	k54	k55	k56	k57	k58	k59	k60	k61	k62	k63
Rock type	Grt	Act	Amp	Grt	Grt	Grt	Diop	Diop	Grt	Grt	Mgm	Diop	Grt	Amp	Amp
Depth (m)	132.20	134.60	136.30	138.40	141.90	143.80	145.70	147.10	148.80	150.20	151.80	152.10	154.80	157.60	158.80
SiO ₂ (wt.%)	70.39	45.23	54.10	57.01	55.73	74.92	55.13	54.38	73.27	56.16	45.40	54.01	76.92	52.46	57.41
TiO ₂	0.49	0.86	0.96	0.53	0.72	0.21	0.90	0.71	0.37	0.76	1.11	0.16	0.04	0.87	0.48
Al ₂ O ₃	10.68	13.82	13.54	12.07	12.42	7.28	12.38	12.66	10.29	13.37	12.11	8.84	9.04	11.40	13.20
FeOt	2.60	9.88	5.53	3.42	1.46	1.64	1.01	2.43	2.18	1.33	9.55	3.09	0.74	6.14	1.35
MnO	0.02	0.18	0.10	0.09	0.04	0.02	0.04	0.06	0.02	0.05	0.15	0.18	0.00	0.14	0.05
MgO	0.54	3.29	2.07	2.51	2.10	0.00	2.04	2.31	0.66	1.88	4.49	2.96	0.00	2.37	1.81
CaO	3.30	11.76	6.01	6.98	9.52	1.91	11.36	9.37	2.69	8.87	5.58	14.76	1.28	6.89	9.22
K ₂ O	1.36	0.81	1.53	1.33	0.46	1.00	0.66	0.53	1.20	0.45	1.76	0.50	2.59	1.14	0.45
P ₂ O ₅	0.13	0.00	0.19	0.27	0.27	0.00	0.16	0.35	0.17	0.00	0.22	0.00	0.14	0.16	0.00
Sum	89.51	85.84	84.03	84.22	82.74	86.97	83.67	82.79	90.85	82.87	80.37	84.49	90.76	81.55	83.97
Ba (ppm)	610	270	620	460	360	310	320	440	1010	330	820	310	450	380	300
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	490	n.d.	n.d.	200
S	n.d.	1940	n.d.	n.d.	130	n.d.	n.d.	n.d.	120	n.d.	140	260	90	n.d.	140
Bi	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.
Cr	120	490	320	230	240	60	210	200	90	250	460	310	50	270	220
Cu	n.d.	200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	20	20	n.d.	n.d.	30	n.d.	20
Rb	30	n.d.	30	40	n.d.	20	n.d.	n.d.	30	n.d.	70	n.d.	40	30	n.d.
Sn	n.d.	n.d.	30	40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	260	170	240	210	250	70	230	290	260	280	130	160	60	210	300
V	150	380	250	210	150	40	150	230	60	170	330	220	n.d.	260	150
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	20	170	40	40	n.d.	n.d.	n.d.	40	30	40	120	70	n.d.	40	20
Zr	320	20	60	40	110	90	50	130	210	130	40	30	60	20	60

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k64	k65	k66	k67	k68	k69	k70	k71	k72	k73	k74	k75	k76	k77
Rock type	Amp	Act	Act	Act	Diop	Amp	Act	Grt	Grt	Grt	Grt	Grt	Grt	Grt
Depth (m)	161.40	162.15	164.00	165.00	166.00	167.60	168.30	171.00	175.40	177.00	179.70	181.50	183.20	186.10
SiO ₂ (wt.%)	50.82	45.30	45.25	51.40	57.84	51.41	51.76	59.64	53.02	56.69	58.09	59.70	59.57	49.84
TiO ₂	1.25	0.63	0.71	0.78	0.84	1.17	0.64	0.66	1.35	0.69	0.66	0.41	0.65	0.48
Al ₂ O ₃	12.04	8.59	8.37	14.88	11.65	12.34	12.17	14.32	11.71	11.87	13.11	12.98	13.87	13.54
FeOt	7.78	9.67	11.24	7.49	2.31	7.35	9.14	4.78	7.52	2.43	1.96	1.30	0.84	3.82
MnO	0.15	0.21	0.23	0.15	0.09	0.11	0.19	0.08	0.11	0.05	0.04	0.03	0.02	0.09
MgO	2.60	6.64	6.44	3.14	3.54	2.63	3.95	1.20	2.16	2.31	1.78	1.58	1.63	2.37
CaO	6.14	12.62	12.25	10.89	11.25	6.38	10.72	6.57	7.00	8.47	9.13	5.32	10.34	6.52
K ₂ O	1.88	0.47	0.69	0.46	0.32	1.32	0.44	0.89	0.57	0.37	0.43	1.78	0.52	0.46
P ₂ O ₅	0.25	0.08	0.14	0.38	0.22	0.18	0.26	0.30	0.25	0.25	0.29	0.22	0.27	0.10
Sum	82.91	84.21	85.31	89.56	88.07	82.90	89.28	88.44	83.70	83.12	85.49	83.33	87.69	77.22
Ba (ppm)	650	210	260	300	290	500	310	250	470	280	350	280	350	220
Cl	n.d.	250	140	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	310	n.d.	n.d.	790	n.d.	440	320	220	150	160	270	n.d.	210	290
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	340	1160	1340	440	340	270	360	190	360	280	250	130	150	250
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	330	360	70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	20	n.d.	n.d.	n.d.	20	n.d.	n.d.	20	20	20	n.d.	n.d.	20	n.d.
Rb	40	n.d.	n.d.	n.d.	n.d.	30	n.d.	20	n.d.	n.d.	n.d.	40	n.d.	20
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30
Sr	220	80	50	370	240	300	270	330	250	250	320	110	320	120
V	310	410	420	320	270	270	390	210	280	230	190	90	120	160
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	80	80	110	60	50	50	70	30	60	30	n.d.	20	20	100
Zr	100	30	30	40	100	30	40	n.d.	240	60	40	70	70	150

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k78	k79	k80	k81	k82	k83	k84	k85	k86	k87	k88	k89	k90	k91	k92
Rock type	Amp	Amp	Amp	Amp	Grt	Mgm	Act	Amp	Act	Act	Amp	Act	Mgm	Mgm	Grt
Depth (m)	187.80	190.24	191.40	194.00	195.80	199.00	200.45	201.30	203.90	206.00	207.50	208.60	212.00	212.00	215.80
SiO ₂ (wt.%)	54.16	53.65	53.90	55.34	59.24	53.64	48.37	66.34	52.18	51.55	60.48	48.83	59.91	56.16	58.59
TiO ₂	0.86	0.90	1.10	1.12	0.28	0.82	0.57	0.66	0.64	0.65	0.61	0.72	0.58	0.81	0.33
Al ₂ O ₃	11.47	11.68	11.50	12.56	13.14	11.91	10.12	10.60	12.46	13.26	10.75	12.55	12.15	11.19	13.23
FeOt	7.40	6.58	7.93	6.74	1.31	0.50	9.29	5.54	9.41	8.88	3.84	9.18	4.71	6.30	4.20
MnO	0.13	0.09	0.14	0.11	0.06	0.00	0.23	0.08	0.21	0.17	0.06	0.19	0.07	0.10	0.10
MgO	2.45	2.14	3.02	2.59	1.46	0.75	5.68	1.97	3.55	2.27	1.26	3.65	1.35	2.50	1.75
CaO	6.73	7.19	7.27	7.30	9.93	6.71	11.89	3.44	9.61	10.51	5.28	11.85	3.44	3.12	7.15
K ₂ O	1.06	1.00	0.91	0.55	0.50	0.47	0.44	1.36	0.60	0.45	1.06	0.48	1.03	1.02	1.33
P ₂ O ₅	0.27	0.20	0.29	0.39	0.17	0.06	0.08	0.20	0.20	0.30	0.29	0.22	0.12	0.22	0.00
Sum	84.54	83.44	86.08	86.71	86.08	74.86	86.66	90.19	88.86	88.04	83.63	87.66	83.37	81.42	86.68
Ba (ppm)	330	380	340	270	310	280	220	450	230	320	480	350	510	500	610
Cl	n.d.	n.d.	110	n.d.	n.d.	n.d.	140	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	150	550	280	160	n.d.	100	n.d.	690	110	n.d.	140	2530	350	180	160
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	300	320	360	310	120	150	1340	260	430	340	220	350	160	300	200
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	100	70	n.d.	n.d.	n.d.	n.d.	240	n.d.	80	100	n.d.	70	n.d.	n.d.	n.d.
Pb	20	20	n.d.	n.d.	20	20	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	n.d.	30
Rb	30	20	30	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	40	30	40
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30
Sr	210	270	200	190	150	200	50	110	140	230	240	260	230	100	180
V	260	240	320	230	110	90	370	230	390	360	190	440	150	220	180
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	70	40	50	70	20	n.d.	100	40	60	60	30	60	60	100	40
Zr	140	100	40	90	60	90	40	40	30	30	330	30	20	100	30

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k93	k94	k95	k96	k97	k98	k99	k100	k101	k102	k103	k104	k105	k106	k107
Rock type	Amp	Amp	Grt	Act	Amp	Amp	Amp	Grt	Grt	Amp	Grt	Amp	Amp	Act	Diop
Depth (m)	217.50	219.60	220.80	222.00	223.00	228.45	231.40	234.00	240.00	241.20	243.30	245.60	247.50	250.30	255.00
SiO ₂ (wt.%)	57.42	49.24	54.63	44.90	48.98	69.73	58.29	74.75	60.80	61.92	76.96	50.22	57.49	42.90	60.68
TiO ₂	0.93	0.62	0.04	0.64	0.54	0.22	0.69	0.14	0.57	0.67	0.11	0.60	0.96	0.69	0.56
Al ₂ O ₃	11.58	14.57	13.22	9.02	14.03	8.98	10.93	8.36	11.66	11.31	9.42	14.34	10.57	10.82	12.71
FeOt	7.91	7.67	0.67	11.56	9.14	2.02	6.40	1.04	1.68	5.11	1.14	8.91	6.00	10.20	1.02
MnO	0.16	0.14	0.00	0.22	0.19	0.03	0.11	0.00	0.05	0.12	0.00	0.20	0.13	0.20	0.05
MgO	2.22	2.36	0.77	6.97	2.89	0.00	1.74	0.00	1.97	2.02	0.00	2.90	2.25	5.78	1.17
CaO	6.70	10.71	8.58	8.69	10.85	1.39	5.17	1.87	6.98	3.86	1.15	11.62	4.12	9.69	6.67
K ₂ O	1.01	0.77	1.61	2.71	0.87	2.30	1.45	1.58	0.51	2.24	3.75	0.55	2.33	2.18	0.46
P ₂ O ₅	0.26	0.08	0.00	0.18	0.17	0.15	0.20	0.11	0.19	0.08	0.08	0.16	0.16	0.00	0.14
Sum	88.20	86.16	79.51	84.90	87.66	84.83	84.99	87.84	84.43	87.34	92.61	89.50	84.01	82.47	83.46
Ba (ppm)	480	340	470	600	390	580	440	580	250	390	1030	290	510	300	310
Cl	n.d.	70	60	140	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	70	n.d.
S	850	180	n.d.	n.d.	220	100	1050	80	170	n.d.	750	710	480	120	n.d.
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	300	250	40	1070	260	80	260	40	160	200	110	260	240	680	160
Cu	40	110	n.d.	n.d.	210	n.d.	80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	370	n.d.	n.d.	n.d.	n.d.	n.d.	70	n.d.	n.d.	n.d.	210	n.d.
Pb	20	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	20	20	40	n.d.	20	n.d.	20
Rb	n.d.	n.d.	40	70	20	30	40	20	n.d.	70	50	n.d.	50	60	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	210	290	80	30	300	80	210	120	180	80	100	310	160	90	190
V	270	380	90	400	340	50	250	30	120	190	50	340	250	400	150
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	60	60	n.d.	100	80	30	50	20	50	70	n.d.	80	60	100	60
Zr	150	20	n.d.	20	30	130	40	130	190	30	80	30	40	n.d.	80

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k108	k109	k110.5	k111	k112	k113	k114	k115	k116	k117	k118	k119	k120	k121	k122
Rock type	Grt	Act	Diop	Diop	Grt	Diop	Diop	Act	Act	Diop	Grt	Diop	Act	Diop	Grt
Depth (m)	256.40	263.00	264.30	267.90	269.50	271.90	274.40	278.85	279.10	282.80	286.20	288.30	294.85	295.70	297.10
SiO ₂ (wt.%)	69.74	48.43	60.63	58.49	64.22	55.00	58.45	42.97	46.27	57.66	68.45	57.33	39.68	57.65	75.04
TiO ₂	0.40	0.66	0.54	0.60	0.04	0.64	0.31	0.54	0.67	0.57	0.30	0.37	0.88	0.45	0.02
Al ₂ O ₃	9.92	10.88	11.42	11.76	10.13	10.55	10.90	8.68	14.64	10.63	10.08	11.54	7.46	11.79	8.57
FeOt	0.04	9.37	2.08	1.83	0.41	1.87	0.85	11.14	8.91	1.93	0.17	0.92	11.00	2.40	0.18
MnO	0.00	0.19	0.09	0.07	0.00	0.10	0.05	0.32	0.19	0.11	0.00	0.03	0.21	0.08	0.00
MgO	0.00	5.01	1.88	1.46	0.00	1.70	1.05	5.21	1.84	2.09	0.00	0.89	4.83	1.61	0.00
CaO	3.56	13.76	7.31	6.91	2.02	6.64	7.72	12.12	10.93	6.90	2.98	9.13	10.21	6.65	0.69
K ₂ O	0.34	0.51	0.56	0.52	2.26	0.54	0.50	1.06	0.64	0.60	0.71	0.87	0.37	0.41	5.17
P ₂ O ₅	0.10	0.00	0.19	0.26	0.00	0.10	0.14	0.14	0.49	0.00	0.00	0.09	0.08	0.16	0.11
Sum	84.10	88.81	84.70	81.91	79.08	77.15	79.97	82.19	84.58	80.48	82.70	81.17	74.70	81.20	89.77
Ba (ppm)	330	250	280	280	590	270	290	380	340	300	340	360	220	260	1800
Cl	n.d.	270	60	n.d.	n.d.	n.d.	n.d.	200	n.d.	n.d.	n.d.	n.d.	110	n.d.	n.d.
S	n.d.	n.d.	n.d.	230	n.d.	280	160	120	360	120	170	100	300	180	n.d.
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	40	810	200	120	60	160	130	1130	210	250	150	150	820	170	40
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	190	n.d.	n.d.	n.d.	n.d.	n.d.	360	100	n.d.	n.d.	n.d.	280	n.d.	n.d.
Pb	20	n.d.	20	20	40	20	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	30
Rb	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	190	210	140	200	130	110	170	40	520	160	150	230	100	220	80
V	n.d.	430	220	140	n.d.	130	140	400	330	200	80	100	420	130	n.d.
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	70	60	40	n.d.	230	30	130	70	50	n.d.	20	160	30	n.d.
Zr	70	20	40	20	50	50	70	20	30	80	30	70	60	110	n.d.

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k123	k124	k125	k126	k127	k128	k129	k130	k131	k132	k133	k137	k138	k139	k140
Rock type	Diop	Diop	Amp	Diop	Diop	Diop	Diop	Diop	Act	Act	Amp	Amp	Grt	Amp	Grt
Depth (m)	299.00	303.00	304.40	306.20	308.80	313.70	316.70	321.20	325.30	326.60	329.90	336.30	337.60	339.30	341.20
SiO ₂ (wt.%)	53.71	57.46	55.48	54.55	55.39	56.36	55.42	56.59	43.55	43.06	49.23	53.42	66.53	56.92	72.17
TiO ₂	0.86	0.53	0.83	0.71	0.60	0.41	0.86	0.83	0.70	0.82	0.87	0.86	0.13	0.79	0.02
Al ₂ O ₃	11.56	13.02	11.15	10.16	11.65	11.75	11.65	11.34	8.40	9.08	9.41	11.24	9.87	12.58	10.40
FeOt	1.85	1.80	2.65	1.51	1.21	0.92	2.80	4.53	10.70	10.96	7.76	7.25	1.11	4.37	0.17
MnO	0.04	0.04	0.08	0.07	0.03	0.00	0.06	0.08	0.22	0.23	0.14	0.10	0.00	0.07	0.00
MgO	1.56	1.41	2.24	2.56	1.74	1.31	1.80	2.42	6.20	4.74	2.61	1.91	0.00	1.58	0.00
CaO	9.62	7.35	8.24	12.11	9.28	9.54	8.41	8.92	12.54	12.70	7.69	7.02	1.42	7.45	2.05
K ₂ O	0.36	0.60	0.59	0.38	0.46	0.41	0.46	0.57	0.75	0.75	0.68	0.93	3.62	0.71	2.51
P ₂ O ₅	0.27	0.23	0.36	0.22	0.25	0.15	0.32	0.22	0.12	0.00	0.14	0.10	0.06	0.24	0.14
Sum	79.83	82.45	81.62	82.26	80.61	80.87	81.78	85.51	83.17	82.35	78.52	82.84	82.74	84.72	87.45
Ba (ppm)	350	280	310	270	210	220	280	280	230	360	280	460	770	350	680
Cl	70	n.d.	n.d.	100	n.d.	n.d.	n.d.	110	110	210	n.d.	n.d.	n.d.	n.d.	n.d.
S	260	120	160	n.d.	270	150	n.d.	n.d.	280	300	100	340	190	260	n.d.
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	270	190	220	270	150	120	240	320	1220	1990	400	270	40	200	120
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	320	240	n.d.	80	n.d.	n.d.	n.d.
Pb	20	20	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	30
Rb	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	20	60	n.d.	50
Sn	n.d.	n.d.	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	240	260	230	190	260	250	240	240	50	170	200	290	110	310	100
V	250	130	240	210	140	160	240	270	370	420	280	260	n.d.	240	50
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	20	30	40	20	n.d.	n.d.	20	20	80	90	50	40	20	30	n.d.
Zr	100	80	80	100	40	70	150	80	30	30	50	30	80	120	40

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

Appendix V continues.

ID	k141	k142	k143	k144	k145	k146	k147	k148	k149	k150	k151
Rock type	Amp	Grt	Diop	Grt	Grt	Amp	Diop	Act	Diop	Act	Diop
Depth (m)	345.00	347.77	349.40	353.00	357.80	362.40	363.30	366.00	367.00	368.00	368.70
SiO ₂ (wt.%)	56.13	79.43	58.43	71.20	70.63	57.49	58.74	45.23	57.09	45.06	58.59
TiO ₂	0.69	0.05	0.69	0.02	0.07	0.44	0.72	0.85	0.63	1.03	0.40
Al ₂ O ₃	12.22	8.31	11.62	11.06	10.39	10.78	12.02	10.27	10.57	11.13	13.32
FeOt	2.83	0.54	1.56	0.23	0.60	1.52	2.72	10.97	1.21	11.73	0.69
MnO	0.06	0.00	0.05	0.00	0.00	0.02	0.06	0.22	0.04	0.24	0.00
MgO	2.15	0.39	2.06	0.00	0.00	1.96	1.64	5.30	1.58	4.90	1.09
CaO	8.42	1.06	7.68	0.83	1.49	7.38	8.13	12.42	9.71	13.08	8.74
K ₂ O	0.48	2.86	0.60	4.56	3.03	0.56	0.56	1.15	0.47	0.83	0.48
P ₂ O ₅	0.26	0.00	0.10	0.00	0.00	0.16	0.10	0.12	0.00	0.14	0.23
Sum	83.25	92.63	82.79	87.90	86.21	80.31	84.69	86.54	81.31	88.14	83.54
Ba (ppm)	330	490	230	540	440	350	310	260	280	310	270
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	120	n.d.	250	680	930	300
S	280	180	n.d.	n.d.	220	100	n.d.	190	110	420	190
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	230	70	210	n.d.	60	210	150	1140	200	990	110
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	260	n.d.	180	n.d.
Pb	n.d.	20	n.d.	30	20	n.d.	n.d.	n.d.	20	n.d.	n.d.
Rb	n.d.	70	n.d.	120	60	n.d.	n.d.	40	n.d.	n.d.	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	220	60	150	60	80	240	240	150	240	210	270
V	260	n.d.	160	n.d.	n.d.	170	180	380	140	490	120
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	20	n.d.	n.d.	n.d.	20	70	20	80	n.d.
Zr	90	60	170	20	70	40	100	30	150	30	20

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Pd, Sb, Se

Rock type names after initial classification. Amp= amphibolite, Grt= granite, Act= actinolite rock, Diop= Diopside-actinolite skarn, Mgm= migmatite

APPENDIX VI: P-XRF data of the outcrop analyses

ID	a1p	a1l	a1p	a1p	a1p	a1p	a1l	a1l	a1l	a1l	a2p	a2p	a2p	a2p	a2p
SiO ₂ (wt.%)	45.42	12.22	44.49	46.03	45.71	45.53	12.37	10.93	12.59	3.08	44.65	46.81	45.82	39.70	42.71
TiO ₂	0.53	0.34	0.53	0.73	1.16	0.74	0.30	0.36	0.27	0.21	0.56	1.08	0.62	1.01	0.66
Al ₂ O ₃	7.01	1.46	6.87	6.85	7.63	7.13	1.62	1.38	1.79	0.36	7.18	6.99	6.79	6.11	7.12
FeOt	1.49	2.64	2.73	1.77	1.99	2.42	2.93	3.30	2.73	2.62	1.21	2.71	2.40	1.77	1.58
MnO	0.06	0.02	0.10	0.07	0.07	0.07	0.03	0.05	0.02	0.02	0.00	0.06	0.05	0.00	0.00
MgO	0.94	0.00	1.19	1.11	1.37	0.74	0.00	0.00	0.00	0.00	0.61	1.04	0.62	0.46	0.55
CaO	4.10	1.02	4.63	4.79	4.55	3.94	1.18	1.28	0.86	1.47	3.44	4.76	3.70	3.81	3.81
K ₂ O	0.94	1.45	1.01	1.01	1.00	1.23	1.51	1.56	1.57	1.11	1.37	1.09	1.02	1.32	1.43
P ₂ O ₅	0.07	0.56	0.14	0.13	0.23	0.14	0.62	0.51	0.52	0.35	0.30	0.22	0.21	0.16	0.23
Sum	60.56	19.71	61.69	62.48	63.72	61.94	20.55	19.38	20.35	9.23	59.31	64.78	61.24	54.35	58.09
Ba (ppm)	280	250	320	280	280	270	220	250	230	220	300	240	290	270	240
Cl	n.d.	1320	100	160	110	n.d.	1380	360	320	450	n.d.	n.d.	n.d.	40	n.d.
S	1150	7440	2190	1390	2040	1790	7690	7800	9090	5420	2170	1860	2080	2480	2130
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	160	160	200	180	220	140	190	190	170	170	130	220	160	190	120
Cu	n.d.	50	n.d.	n.d.	n.d.	n.d.	40	30	70	70	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	40	70	50	40	70	50	70	70	80	70	30	40	40	50	40
Rb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	30	n.d.	n.d.	n.d.	n.d.	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	130	130	140	120	150	150	120	100	100	100	230	90	140	210	230
V	140	120	170	190	180	130	130	160	120	100	110	200	140	160	140
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	30	150	80	30	50	60	170	140	190	130	n.d.	90	20	20	n.d.
Zr	80	100	70	90	190	90	110	70	100	110	60	60	120	100	80

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	a2l	a2l	a2l	a2l	a2l	a3p	a3p	a3p	a3p	a3p	a3l	a3l	a3l	a4p	a4p
SiO ₂ (wt.%)	34.77	11.44	19.56	7.91	23.06	40.95	43.81	42.83	45.55	48.03	10.28	8.50	9.28	66.05	62.44
TiO ₂	0.45	0.42	0.48	0.27	0.50	0.80	1.37	0.71	1.26	0.90	0.32	0.24	0.34	0.09	0.11
Al ₂ O ₃	4.81	1.43	2.48	0.99	3.12	6.59	7.46	7.16	7.85	7.96	1.08	1.03	1.34	8.66	6.33
FeOt	3.06	2.24	2.73	2.39	3.03	1.32	2.27	2.79	2.23	1.69	2.23	2.57	3.21	0.22	0.40
MnO	0.07	0.02	0.03	0.00	0.05	0.03	0.04	0.04	0.04	0.04	0.00	0.00	0.03	0.00	0.00
MgO	0.00	0.00	0.55	0.00	0.00	0.51	0.77	0.68	1.01	1.07	0.00	0.00	0.00	0.52	0.40
CaO	3.25	1.19	1.57	2.03	1.82	3.38	4.86	4.20	4.49	5.15	0.96	0.72	1.40	1.25	0.85
K ₂ O	1.47	1.50	1.62	1.59	1.47	1.20	1.14	1.17	0.88	1.29	1.55	1.41	1.69	2.58	3.14
P ₂ O ₅	0.34	0.44	0.47	1.50	0.47	0.17	0.10	0.05	0.16	0.18	0.44	0.56	0.61	0.11	0.21
Sum	48.22	18.67	29.48	16.69	33.52	54.94	61.83	59.63	63.48	66.32	16.85	15.03	17.91	79.48	73.88
Ba (ppm)	270	300	230	210	320	270	280	300	300	240	270	240	290	580	690
Cl	70	270	1100	300	930	n.d.	n.d.	n.d.	n.d.	n.d.	840	910	170	n.d.	n.d.
S	4780	7150	6030	7000	5870	2430	560	580	790	1300	4890	5490	8950	850	2550
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	190	180	160	140	180	90	180	190	160	130	150	170	180	60	60
Cu	n.d.	n.d.	30	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	40	40	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	40	50	50	40	60	40	50	40	40	30	50	70	40	30	30
Rb	n.d.	20	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	50
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	150	130	210	140	150	200	210	180	210	230	160	130	170	80	70
V	180	130	160	90	170	120	180	230	150	200	110	110	140	50	n.d.
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	90	n.d.	n.d.	n.d.
Zn	50	80	100	80	90	20	40	40	n.d.	20	130	170	100	n.d.	n.d.
Zr	200	80	130	100	100	40	30	40	30	170	40	120	80	50	n.d.

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	a4p	a5p	a5p	a5p	a5p	a5l	a5l	a5l	b1p	b1p	b1p	b1p	b1p	b1p	b1p
SiO ₂ (wt.%)	62.52	47.06	57.66	48.34	66.59	19.88	25.46	12.08	47.58	52.73	57.45	54.41	53.20	59.82	57.83
TiO ₂	0.17	0.62	0.10	0.85	0.08	0.24	0.27	0.24	1.23	0.74	0.46	0.35	0.79	0.23	0.76
Al ₂ O ₃	6.16	8.03	6.07	8.04	7.23	2.12	2.91	1.44	10.27	10.03	4.48	7.08	9.51	8.33	9.41
FeOt	0.72	1.10	0.28	1.17	0.21	0.84	0.95	1.19	5.58	2.07	1.98	1.92	5.52	0.79	3.22
MnO	0.00	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.12	0.06	0.00	0.00	0.10	0.00	0.03
MgO	0.36	0.61	0.35	0.79	0.00	0.00	0.00	0.00	1.95	1.20	0.40	0.00	1.40	0.66	0.00
CaO	1.26	7.51	1.12	3.42	1.09	0.96	1.19	0.65	7.68	7.27	1.46	1.92	4.26	3.54	3.44
K ₂ O	1.57	0.73	1.87	1.04	1.79	1.61	1.60	1.50	0.54	0.81	1.18	2.53	1.72	0.53	1.59
P ₂ O ₅	0.19	0.16	0.33	0.20	0.21	0.51	0.50	0.59	0.38	0.00	0.12	0.09	0.40	0.17	0.21
Sum	72.94	65.85	67.78	63.88	77.20	26.17	32.88	17.70	75.33	74.92	67.52	68.29	76.90	74.08	76.48
Ba (ppm)	360	310	680	280	600	630	710	590	280	250	400	640	320	230	810
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	650	230	170	n.d.	n.d.	n.d.	n.d.	180	n.d.	n.d.
S	1760	920	4590	1770	3350	6010	7240	8140	510	420	500	780	2310	850	730
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	60	170	110	150	20	120	140	150	290	160	70	110	220	n.d.	60
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	30	n.d.	40	40	40	40	30	50	n.d.	20	20	20	20	20	30
Rb	30	n.d.	30	n.d.	20	30	30	30	n.d.	n.d.	40	50	60	n.d.	50
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	70	240	80	110	90	70	90	60	320	210	140	210	190	150	300
V	50	140	n.d.	130	n.d.	60	70	80	330	200	n.d.	100	200	90	80
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	50	60	70	40	20	20	20	50	n.d.	50
Zr	50	120	30	50	40	40	50	40	20	30	150	190	90	110	300

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	b1l	b1l	b1l	b1l	b1l	b1l	b1l	c1p	c1l	c2p	c2l	c3p	c3l	c4p	c4l
SiO ₂ (wt.%)	17.37	20.93	16.27	14.78	12.84	14.21	18.95	44.90	26.18	50.76	28.20	47.98	20.98	49.10	31.39
TiO ₂	0.47	0.48	0.19	0.20	0.42	0.17	0.38	0.83	0.69	0.50	0.46	0.65	0.68	0.82	0.46
Al ₂ O ₃	2.43	2.68	1.70	1.57	1.64	1.76	2.49	7.51	3.66	8.77	3.87	7.60	2.88	8.79	4.94
FeOt	3.85	2.58	1.07	1.36	4.51	1.13	2.39	5.44	3.60	1.56	2.32	1.30	1.80	2.98	4.63
MnO	0.05	0.08	0.00	0.00	0.06	0.02	0.00	0.12	0.06	0.02	0.04	0.05	0.05	0.07	0.09
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.28	0.00	0.41	0.00	0.59	0.00	0.65	0.58
CaO	2.00	2.97	1.10	0.97	1.80	1.42	2.06	4.62	2.41	4.75	2.42	5.21	2.66	4.49	2.42
K ₂ O	1.80	1.54	1.61	1.81	1.78	1.54	2.45	1.04	1.64	0.68	1.36	0.76	1.10	0.42	1.11
P ₂ O ₅	0.57	0.46	0.37	1.16	0.70	0.85	0.88	0.42	0.37	0.23	0.26	0.22	0.39	0.15	0.36
Sum	28.55	31.72	22.30	21.85	23.75	21.11	29.59	66.15	38.60	67.69	38.92	64.37	30.54	67.46	45.97
Ba (ppm)	260	250	1090	480	240	180	1620	410	380	250	220	310	300	240	400
Cl	1140	960	900	860	600	320	900	n.d.	70	n.d.	80	n.d.	100	n.d.	110
S	10250	8300	5550	10360	6880	9980	7750	1460	6070	950	4460	1380	5710	870	6360
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	210	220	110	130	200	100	150	260	200	100	180	150	160	100	180
Cu	50	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	50	60	30	20	40	30	60	20	80	20	50	n.d.	30	20	40
Rb	n.d.	60	40	30	40	n.d.	50	20	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	280	190	180	210	170	140	310	150	140	160	160	160	190	180	180
V	160	170	50	50	170	80	130	250	210	100	140	160	150	150	160
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	220	80	70	90	170	100	80	60	60	40	50	n.d.	40	40	60
Zr	50	40	90	150	80	110	200	100	120	100	100	90	70	80	60

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	c5p	c5l	d1p	d1l	d2p	d2l	dx	e1p	e1l	e1l	e2p	e2l	f1p	f1l	f2p
SiO ₂ (wt.%)	52.27	37.38	47.19	11.97	63.58	31.45	73.77	52.02	32.85	36.46	48.16	21.89	53.07	38.02	61.93
TiO ₂	0.56	0.67	0.57	0.27	0.08	0.16	0.02	0.70	0.50	0.62	0.84	0.39	0.54	0.22	0.10
Al ₂ O ₃	8.45	5.42	6.73	1.59	5.11	2.31	9.15	7.94	4.39	4.89	7.80	2.41	9.15	8.40	8.36
FeOt	5.24	4.28	4.11	3.01	0.56	0.83	0.05	5.31	3.82	5.11	6.20	3.20	4.67	11.23	1.56
MnO	0.12	0.11	0.07	0.02	0.00	0.00	0.00	0.05	0.03	0.06	0.14	0.05	0.08	0.05	0.05
MgO	0.91	0.60	0.48	0.00	0.00	0.00	0.00	1.06	0.00	0.88	0.99	0.00	1.21	2.33	0.60
CaO	5.50	3.40	4.51	0.99	2.70	2.02	0.09	3.94	3.84	3.26	5.21	4.09	6.30	0.64	0.22
K ₂ O	0.77	1.18	0.94	1.60	0.71	1.22	6.60	1.31	0.96	1.18	0.63	1.06	0.43	2.61	7.36
P ₂ O ₅	0.37	0.30	0.29	0.77	0.54	0.75	0.00	0.38	0.52	0.46	0.23	1.62	0.07	0.38	0.06
Sum	74.18	53.34	64.88	20.22	73.28	38.73	89.69	72.73	46.92	52.92	70.19	34.72	75.53	63.87	80.24
Ba (ppm)	370	400	360	340	310	230	520	690	490	510	330	380	240	810	410
Cl	n.d.	n.d.	70	990	n.d.	640	n.d.	n.d.	n.d.	110	n.d.	250	n.d.	n.d.	n.d.
S	2240	3350	2070	5170	2210	4010	1930	820	5370	3830	1380	8880	180	950	340
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	260	200	140	150	70	150	n.d.	140	110	180	200	130	210	280	80
Cu	n.d.	n.d.	n.d.	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	80	n.d.
Pb	n.d.	n.d.	20	50	20	30	70	n.d.	n.d.	n.d.	n.d.	20	n.d.	20	60
Rb	n.d.	20	30	20	n.d.	n.d.	100	30	20	20	20	30	n.d.	70	50
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	250	180	210	160	190	160	50	190	220	190	230	230	230	70	40
V	210	180	120	120	n.d.	n.d.	n.d.	140	170	160	160	110	180	370	50
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	60	50	120	160	30	30	n.d.	60	20	30	30	50	30	60	50
Zr	110	90	80	90	90	40	n.d.	120	100	100	110	90	120	50	50

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	f2p	f3p	f3l	f4p	f5p	f5l	g1l	g2l	g1p	h1l	h2l	h3l	h4l	h5l
SiO ₂ (wt.%)	62.63	60.26	42.17	39.88	55.89	31.59	32.34	25.48	36.09	69.10	51.27	64.56	68.56	47.38
TiO ₂	0.10	0.04	0.12	0.90	0.61	0.57	0.47	0.48	0.72	0.15	0.19	0.16	0.09	1.26
Al ₂ O ₃	4.65	6.91	3.31	5.72	9.98	5.14	4.00	3.45	4.76	7.35	4.69	7.45	6.92	9.00
FeOt	0.58	0.47	0.72	4.69	6.87	5.67	3.30	4.65	4.89	1.27	1.33	1.17	0.74	7.17
MnO	0.00	0.00	0.00	0.12	0.12	0.08	0.05	0.06	0.08	0.00	0.00	0.00	0.00	0.13
MgO	0.00	0.55	0.00	0.76	1.25	0.00	0.00	0.00	0.63	0.72	0.00	0.00	0.00	1.54
CaO	1.04	0.84	1.30	3.88	4.41	3.07	3.62	6.08	3.31	0.93	1.47	1.11	1.03	5.35
K ₂ O	1.02	3.87	2.20	1.86	0.56	1.26	1.17	1.49	0.92	2.91	2.31	3.00	2.68	2.38
P ₂ O ₅	0.25	0.38	0.38	0.68	0.26	0.31	0.41	0.45	0.33	0.11	0.45	0.21	0.06	0.36
Sum	70.27	73.32	50.21	58.50	79.95	47.70	45.36	42.15	51.71	82.54	61.72	77.65	80.07	74.57
Ba (ppm)	140	270	250	540	410	300	410	570	380	480	510	500	480	480
Cl	n.d.	n.d.	n.d.	150	n.d.	350	210	80	230	n.d.	n.d.	n.d.	n.d.	n.d.
S	1930	1670	3410	2760	770	4350	2930	3670	1960	320	3360	1910	520	1760
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	50	20	80	200	230	210	120	160	190	50	60	n.d.	60	290
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	20	30	20	n.d.	n.d.	20	n.d.	20	n.d.	40	30	30	20	n.d.
Rb	n.d.	50	40	110	n.d.	n.d.	n.d.	30	20	60	60	60	60	120
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	40	30	40	180	170	140	210	200	210	60	70	80	70	200
V	50	50	30	190	180	190	80	170	160	50	n.d.	n.d.	n.d.	280
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	30	120	30	80	40	100	30	20	30	20	n.d.	60
Zr	40	20	40	110	70	90	100	120	120	70	100	60	50	70

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	h6l	h6p	h6.5p	i1l	i1p	j1l	j2l	j2p	j1p	j3l	j3p	j4p	j4l	j5l	j5p
SiO ₂ (wt.%)	42.09	52.42	55.75	26.56	47.81	66.40	57.12	52.17	63.85	40.09	45.71	43.40	32.52	49.71	59.40
TiO ₂	0.81	0.62	0.96	0.37	0.90	0.38	0.76	0.81	0.44	0.65	0.84	0.58	0.58	0.79	1.01
Al ₂ O ₃	7.42	7.66	7.71	3.53	7.93	7.66	9.30	9.84	9.84	5.70	7.46	10.28	4.15	7.03	11.16
FeOt	8.16	4.93	5.36	4.42	5.82	2.14	5.15	5.78	2.83	4.98	5.46	10.14	9.64	6.50	5.67
MnO	0.09	0.09	0.06	0.11	0.12	0.02	0.11	0.11	0.03	0.12	0.10	0.20	0.20	0.11	0.06
MgO	2.59	0.62	1.49	0.00	2.25	0.00	1.36	1.73	0.47	1.04	1.37	5.02	0.00	0.76	1.34
CaO	2.41	4.83	2.92	3.76	7.37	2.22	5.35	6.17	2.41	5.92	5.36	10.62	8.97	5.55	6.14
K ₂ O	2.91	1.01	2.27	1.80	0.31	1.12	1.14	0.41	1.37	0.70	1.19	0.78	1.02	1.21	0.56
P ₂ O ₅	0.52	0.38	0.19	0.97	0.29	0.42	0.35	0.24	0.19	0.41	0.24	0.00	1.13	0.57	0.29
Sum	67.01	72.56	76.71	41.52	72.81	80.36	80.64	77.24	81.42	59.61	67.73	81.03	58.21	72.22	85.64
Ba (ppm)	400	410	380	230	320	700	360	350	820	300	270	330	370	340	280
Cl	n.d.	120	n.d.	490	130	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	170	470	50	n.d.
S	2610	1890	170	6310	100	2860	3250	640	170	2180	340	210	6310	3430	100
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	440	200	220	210	340	60	200	200	50	210	210	610	680	150	150
Cu	50	n.d.	n.d.	70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	210	170	n.d.	n.d.
Pb	20	n.d.	n.d.	50	20	70	40	n.d.	20	n.d.	n.d.	n.d.	n.d.	20	n.d.
Rb	40	20	60	n.d.	n.d.	20	20	n.d.	30	n.d.	n.d.	20	30	n.d.	n.d.
Sn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.
Sr	120	210	150	260	240	220	180	200	240	200	210	120	90	170	220
V	290	170	190	150	290	50	200	200	70	230	160	370	300	300	380
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	210	40	50	150	50	30	50	60	30	40	40	80	300	70	n.d.
Zr	130	40	90	60	70	190	70	60	330	60	50	20	n.d.	90	70

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

Appendix VI continues.

ID	j6l	j6p	k1l	k1p	k2p	k2l	k3l	k3p	k4p	k4l
SiO ₂ (wt.%)	55.78	67.29	39.52	52.93	44.58	42.10	40.24	75.10	56.72	67.60
TiO ₂	0.15	0.12	0.25	1.54	1.34	1.08	0.36	0.42	0.60	0.34
Al ₂ O ₃	5.39	6.99	4.10	11.97	10.35	7.51	3.36	6.18	6.37	8.71
FeOt	1.01	1.00	2.36	4.37	11.53	10.36	2.45	2.17	3.80	2.65
MnO	0.02	0.00	0.02	0.03	0.19	0.18	0.03	0.03	0.04	0.03
MgO	0.00	0.75	0.46	1.37	2.06	0.00	0.00	0.00	0.71	0.47
CaO	2.21	1.06	2.87	5.27	7.88	6.75	2.77	2.24	2.48	2.96
K ₂ O	1.70	2.72	0.98	1.78	0.61	0.77	1.49	1.09	1.70	1.20
P ₂ O ₅	0.49	0.11	0.64	0.38	0.57	0.43	0.71	0.17	0.16	0.19
Sum	66.75	80.03	51.20	79.63	79.11	69.18	51.41	87.40	72.59	84.15
Ba (ppm)	470	350	930	910	320	380	470	550	480	510
Cl	n.d.	n.d.	180	n.d.	n.d.	470	250	n.d.	n.d.	n.d.
S	4500	170	5200	n.d.	840	4600	6350	n.d.	n.d.	2350
Bi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	80	40	150	210	240	180	100	110	110	90
Cu	n.d.	n.d.	n.d.	n.d.	60	70	40	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	30	20	60	n.d.	n.d.	n.d.	20	n.d.	n.d.	20
Rb	40	40	30	30	n.d.	n.d.	30	30	30	30
Sn	n.d.	n.d.	30	40	50	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	70	60	440	430	250	230	150	170	130	150
V	n.d.	40	n.d.	160	420	370	90	50	130	100
W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	40	n.d.	70	50	100	180	100	30	20	60
Zr	50	70	260	280	70	70	130	80	110	110

Excluded elements (all values <LOD): Ag, Au, As, Cd, Co, Mo, Nb, Pd, Sb, Se

First letter in the ID indicates the outcrop. l= poor quality surface, p= good quality surface.

APPENDIX VII: Geochemical data of the temporally related amphibolite units

Appendix VII. Data from GTK bedrock geochemical database of Finland. Data obtained with WD-XRF with pressed powder pellets and ICP-MS (Rasilainen et al. 2007).

WD-XRF							
Point ID	1	2	3	4	5	6	7
X coordinate	6670600	6667290	6679410	6678790	6684450	6721620	6701070
Y coordinate	3338950	3353710	3367860	3375200	3386690	3415650	3435860
Location	Inkoo	Kirkkonummi	Espoo	Espoo	Helsinki	Sääksjärvi	Porvoo
Rocktype	Amp.	Amp.	Amp.	Amp.	M. volc.	Amp.	M. volc.
SiO ₂ (wt. %)	45.40	47.10	53.00	50.70	51.40	50.10	43.00
TiO ₂	2.70	0.64	0.62	2.38	0.96	1.77	2.44
Al ₂ O ₃	12.10	15.60	16.70	13.80	16.70	15.90	13.00
FeO _t	15.93	7.77	7.76	13.32	9.90	8.73	11.25
MnO	0.26	0.16	0.16	0.24	0.19	0.15	0.17
MgO	5.24	8.57	4.36	3.41	3.96	4.24	5.53
CaO	8.22	11.60	8.09	7.16	6.62	7.69	11.40
Na ₂ O	2.19	1.74	2.75	3.06	4.77	3.63	3.62
K ₂ O	1.07	0.28	0.68	0.83	0.72	1.62	0.85
P ₂ O ₅	0.12	0.03	0.10	0.24	0.20	0.93	0.30
Sum	93.23	93.48	94.21	95.13	95.42	94.76	91.55
Ba (ppm)	163	61.8	213	179	392	596	459
Cl	741	141	261	483	80.1	505	146
S	220	737	114	591	78	2270	1500
Cr	<19	491	47.1	27	24	27	96.1
Cu	30.1	72	17	33.9	<17	129	188
Ga	22	19	23.2	23.7	29	29.8	31.4
Nb	<7	<7	<7	7.6	<7	22.5	45.9
Ni	<14	103	<14	15	<14	38.4	122
Pb	16	<14	22	23	27	16	15
Rb	66.1	14.6	15.3	20.7	33.1	141	29
Sr	121	153	272	149	224	1200	323
V	974	185	184	459	209	221	395
Y	30.6	9.1	16	46.7	17.4	20.3	21.3
Zn	175	77	92.3	135	131	141	121
Zr	84.8	21	70.5	194	115	186	195
Mo excluded (all values <LOD)							
ICP-MS							
Ce (ppm)	21.20	4.64	21.70	34.30	34.70	95.20	64.30
Co	48.8	42.4	26.2	33.4	29.9	32.7	51.4
Dy	4.93	2.01	2.81	7.39	3.94	4.40	4.88
Er	3.18	1.13	1.53	5.06	2.09	1.66	2.29
Eu	0.97	0.64	0.81	1.77	1.39	2.50	2.07
Gd	4.23	1.84	3.06	7.06	4.27	7.77	6.49
Hf	2.18	0.63	2.00	4.60	2.94	2.91	4.50
Ho	1.05	0.44	0.58	1.77	0.73	0.73	0.87
La	9.74	1.82	10.50	16.40	16.20	43.30	30.70
Lu	0.44	0.16	0.22	0.74	0.32	0.23	0.27
Nb	4.66	0.62	3.42	8.42	6.58	16.90	38.50
Nd	12.30	4.08	11.90	20.60	19.50	50.40	31.30
Pr	2.87	<0.74	2.85	4.78	4.58	12.20	7.76
Rb	55.0	13.8	14.7	17.3	35.3	129.0	31.1
Sc	59.5	43.4	35.7	44.5	35.6	17.9	35.0
Sm	3.46	1.40	2.72	5.62	4.23	9.27	6.46
Ta	0.40	0.06	0.29	0.59	0.43	0.84	2.19
Tb	0.79	0.31	0.45	1.23	0.59	0.98	0.90
Th	1.34	0.24	2.37	2.01	3.04	3.69	3.44
Tm	0.48	0.21	0.26	0.74	0.32	0.25	0.32
U	1.06	<0.08	0.74	0.84	1.56	1.87	0.69
V	911.0	177.0	177.0	413.0	193.0	195.0	354.0
Y	31.80	11.80	16.20	49.20	20.50	22.60	26.00
Yb	3.18	1.15	1.70	5.03	1.99	1.59	1.94
Zr	78.8	18	64.7	177	113	148	170

Amp.=amphibolite

M.volc.=mafic volcanite